SAND2014-4427C

Atomic Scale Investigation of Interfaces and Dislocations in Telluride-Based Thermoelectric Materials

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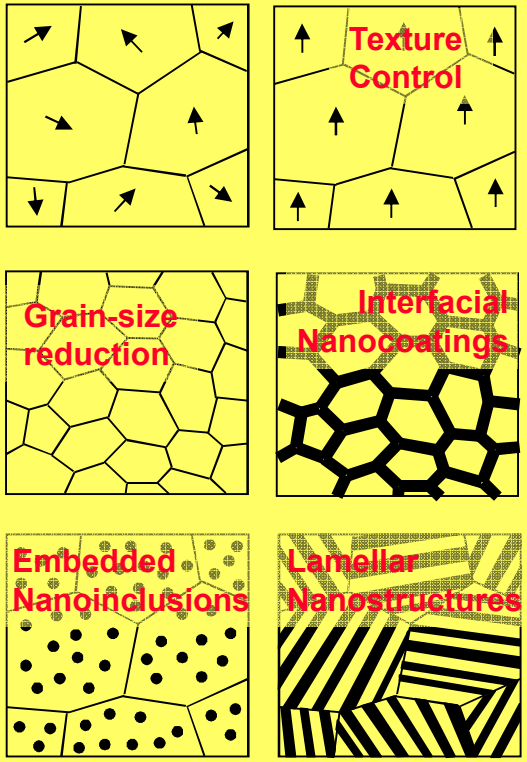
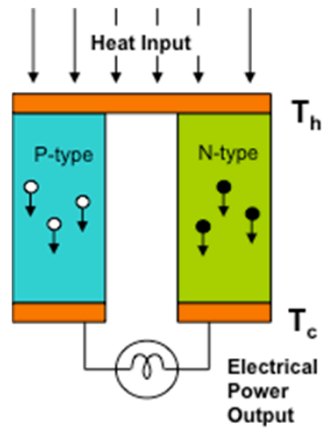
Thermoelectric Materials: Important Roles for Interface Science

Microstructural Strategies for Nanostructured Bulk Thermoelectrics



Medlin and Snyder, Current Opinion in Colloid and Interface Science, 2009

Thermoelectric Power Generation



Seebeck Coefficient

Electrical Conductivity

$$zT = \frac{\alpha^2 \sigma}{\kappa} T$$

Thermal Conductivity

- ***Interfacial strategies to enhance zT***
  - **-phonon scattering:** $\downarrow \kappa$
  - **-energy filtering:** $\uparrow \alpha^2 \sigma$
- ***Interfaces must remain stable:***
  - **-nanoscale separations.**
  - **-elevated temperature.**

Interfacial structure underpins transport properties and stability

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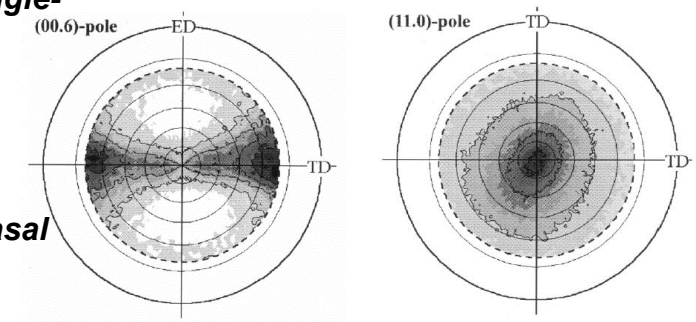
Improved Thermoelectric Performance Through Tailored Interfaces

Control of Crystal texture

Example: Texture in Hot Extruded Bi_2Te_3

Anisotropic single-crystal TE properties

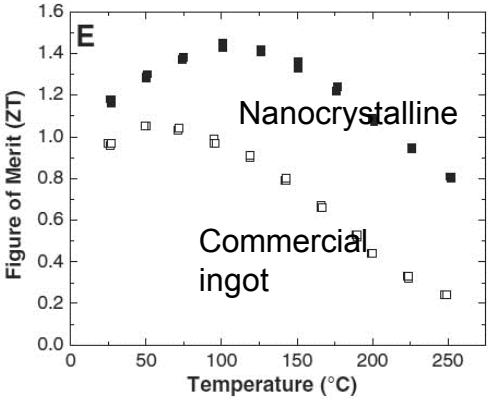
Highest zT for transport Parallel with basal planes

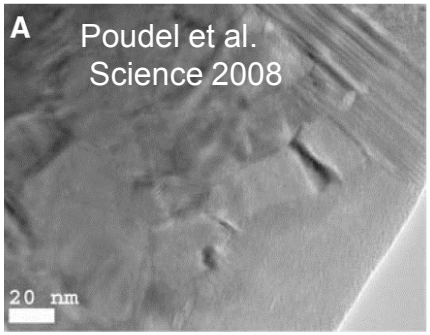


Miura et al., Mat. Sci. Eng. A (2000)

Reduction of Grain Size

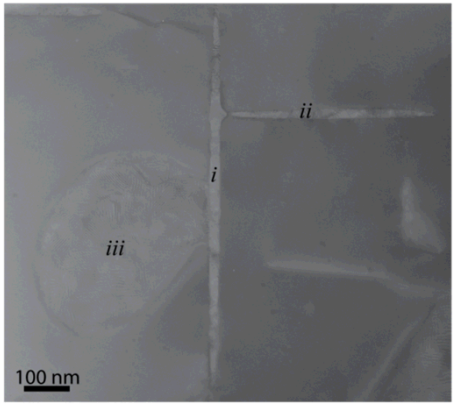
Example: Enhanced zT in nanocrystalline $(Bi,Sb)_2Te_3$

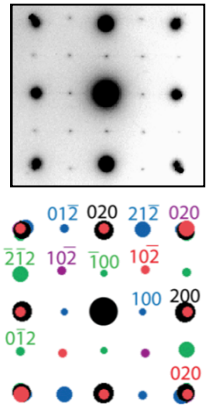




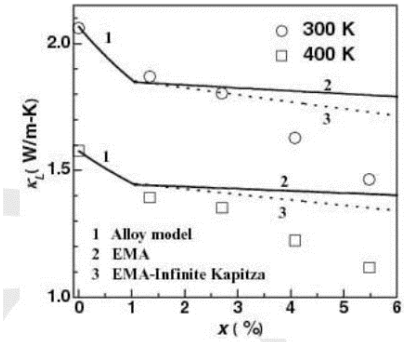
Embedded Nanoprecipitates

Example: Ag_2Te precipitates in PbTe

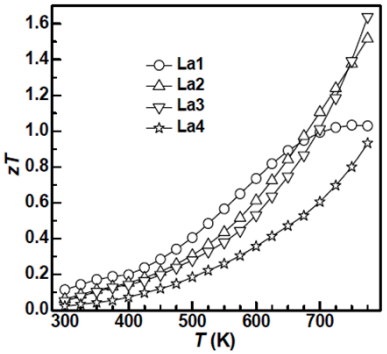




Phonon scattering on Ag_2Te precipitates lowers κ_L



zT as high as 1.6 with suitable doping

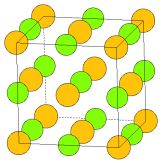


J. Lensch-Falk, J. Sugar, M. Hekmaty, D. Medlin, Journal of Alloys and Compounds (2010)

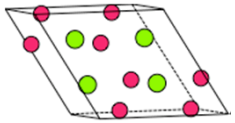
Y. Pei, J. Lensch-Falk, E.S. Toberer, D.L. Medlin, G.J. Snyder, *Advanced Functional Materials* (2011).

Our focus: Extended Defects in Chalcogenides

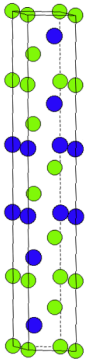
Rock-Salt
($PbTe$, $AgSbTe_2$)



Monoclinic
(Ag_2Te)



Tetradymite
(Bi_2Te_3,Sb_2Te_3)



Rich set of structures and phase relations

Longstanding importance as thermoelectrics

-Bi_2Te_3-based alloys widely used for cooling, some low grade waste heat recovery applications

-p-type : $(Bi_{0.2}Sb_{0.8})_2Te_3$

-n-type $Bi_2(Te_{0.9}Se_{0.1})_3$

-PbTe and $(GeTe)_x(AgSbTe_2)_{1-x}$):

-higher T application

-unattended operation.

Emerging interest as topological insulators

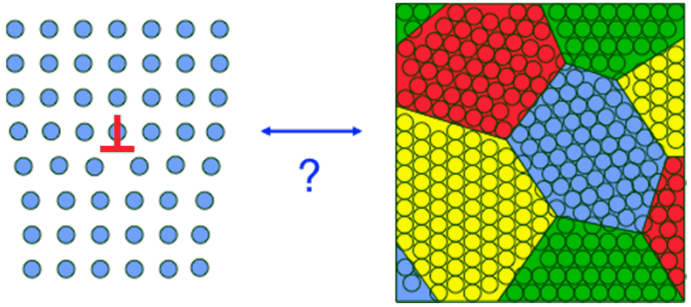
-Bi_2Se_3

Can we begin to make sense of interfaces in these complex systems?

Our approach:

Understand structural relationships between chalcogenide phases.

Determine basic elements of interfacial structure.



Dislocations and Interfacial Line Defects:

Building blocks to general understanding of interface structure and behavior.

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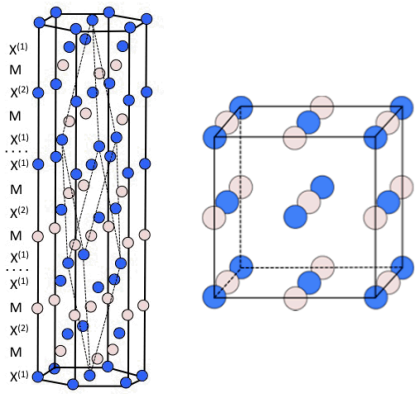
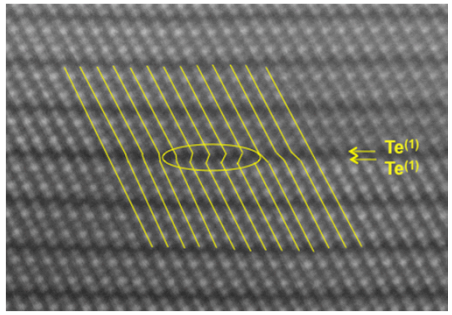
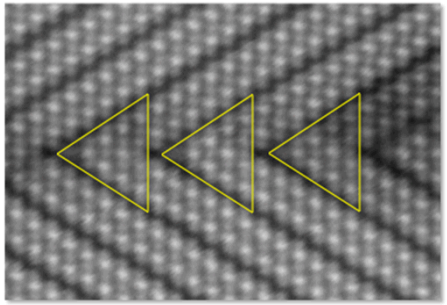
Outline

- *Crystal structure in tetradymite-type compounds*
  - Layered structure gives flexibility in accommodating compositional variations
  - Close structural relationship to rock-salt chalcogenides

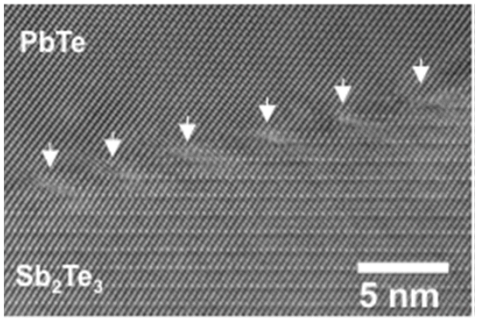


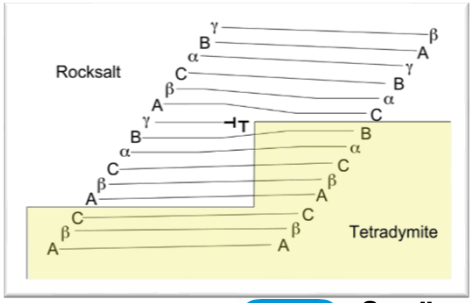
- *Dislocation and Grain Boundary Structure in Bi_2Te_3*
  - Impact of weak interlayer bonding
  - local rocksalt coordination





- *Rocksalt/Tetradymite heterophase interfaces:*
  - Interfacial disconnections at Sb_2Te_3 precipitates in $AgSbTe_2$, and PbTe.
  - Defect roles in mechanisms for phase transformation and strain accommodation





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Collaborators

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LBNL/NCEM

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California Institute of Technology

N.A. Heinz, T. Ikeda, G.J. Snyder

Special thanks to:

-LLNL: John Bradley, for use for LLNL's Titan 80/300 instrument
-LBNL: User program, National Center for Electron Microscopy
-UCD: Z. Zhang and E. Lavernia, for assistance with bulk Bi_2Te_3 processing

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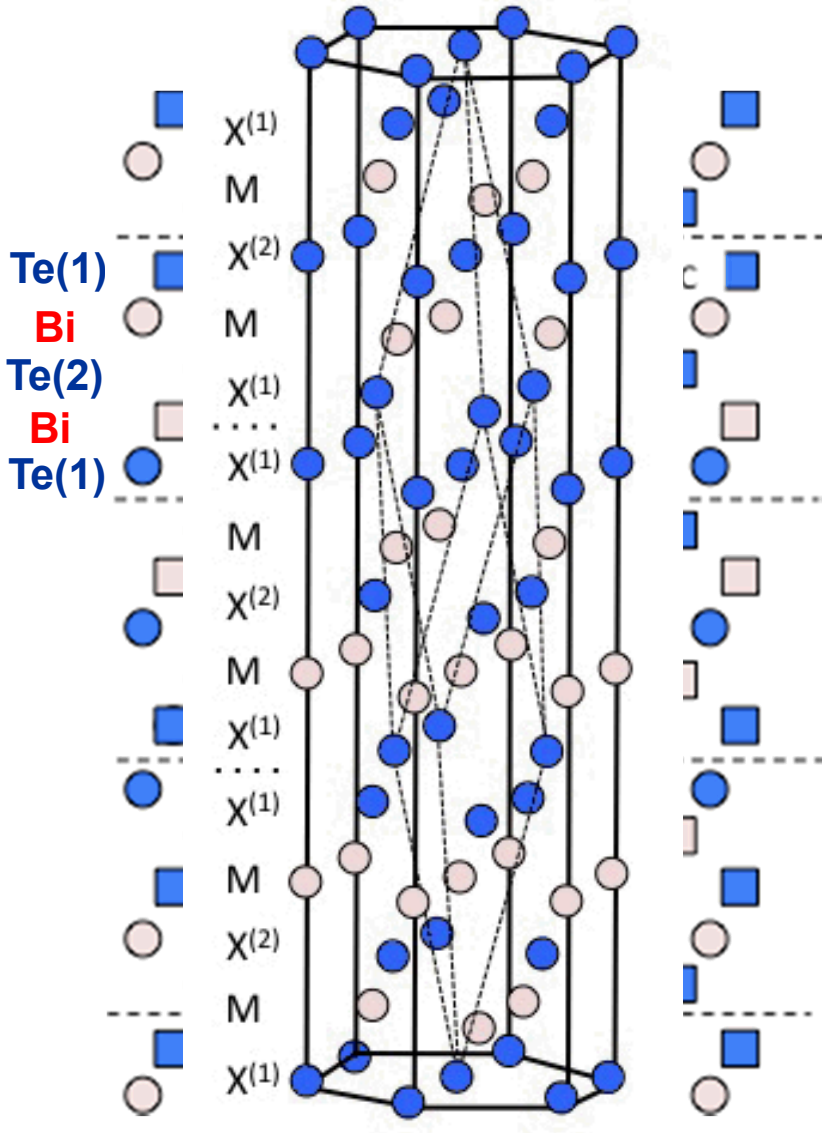
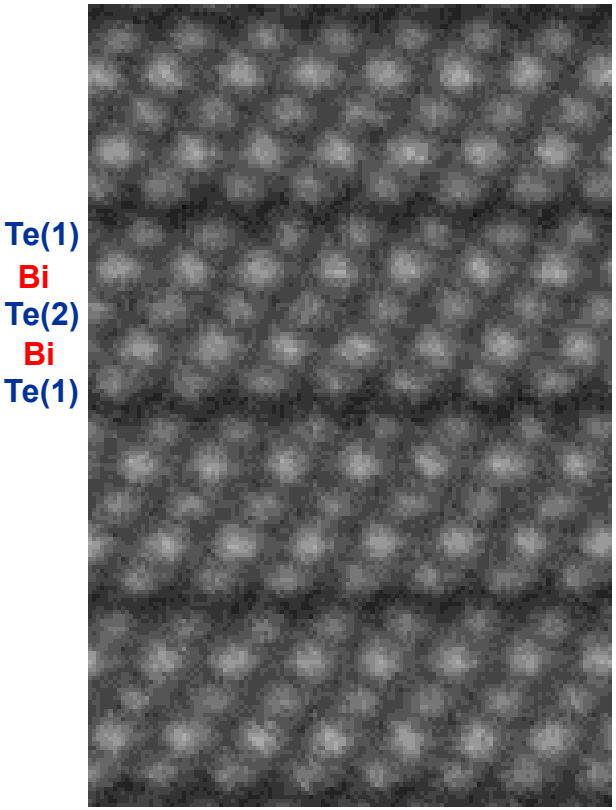
Bismuth Telluride (Bi_2Te_3): Crystal Structure



- Rhombohedral (R-3m) structure
- Based on tetradymite (Bi_2STe_2) prototype
- Three crystallographically distinct atomic sites
- $Te^{(1)}$-$Te^{(1)}$ layers: van der Waals bonding

HAADF-STEM



Bi: Z=83
Te: Z=52

Atomic number difference enables Bi and Te to be distinguished in HAADF-STEM

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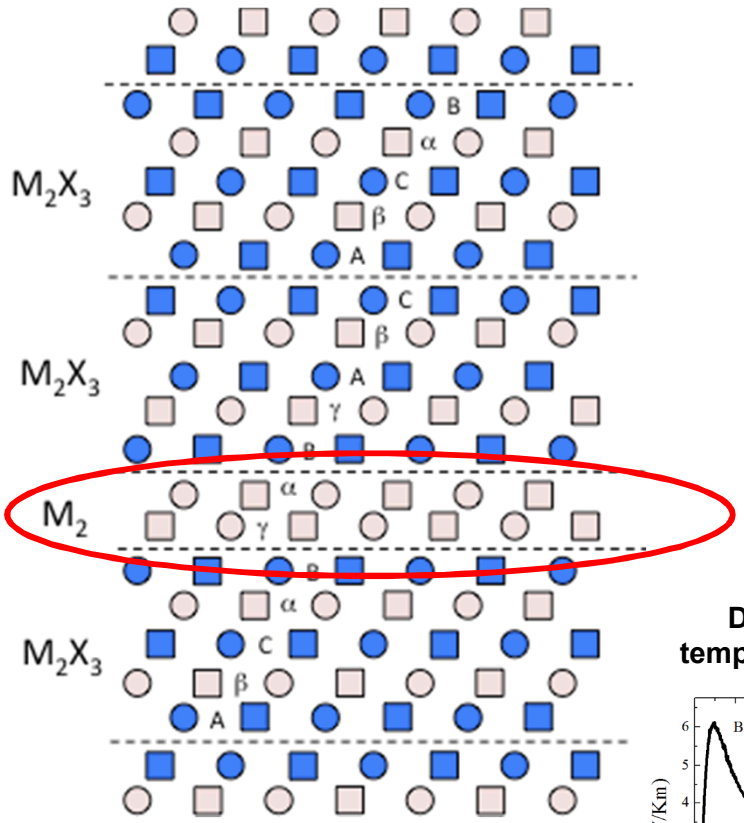
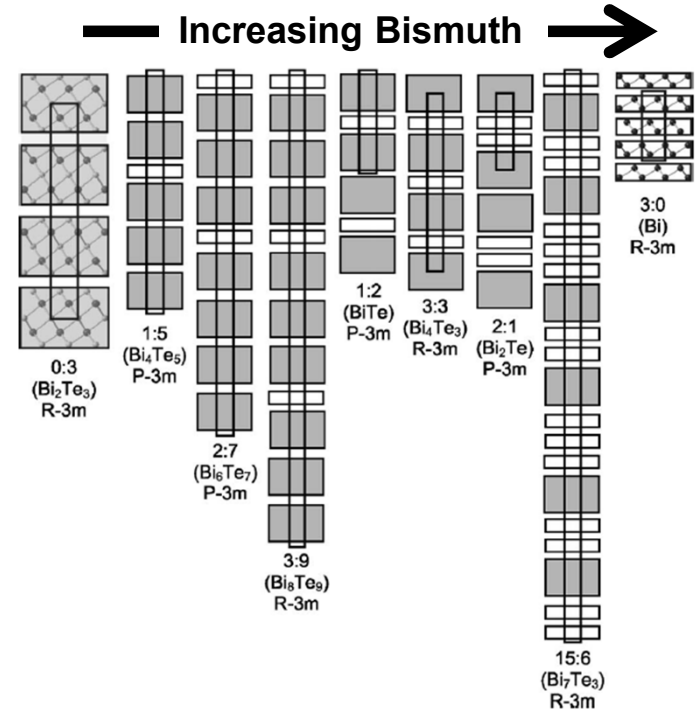
Layered structure allows flexibility in accommodating variations in composition

Insertion of metal bi-layers

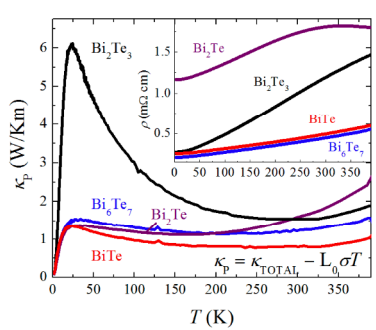


Example: $(Bi_2)_m(Bi_2Te_3)_n$ homologous series

J.W.G. Bos, H.W. Zanderbergen, M.-H. Lee, N.P. Ong, R.J. Cava, Phys. Rev B 2007

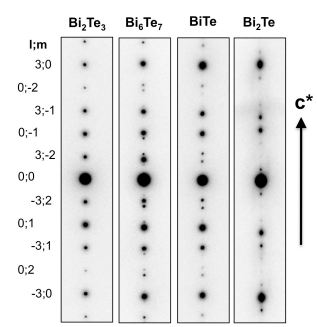


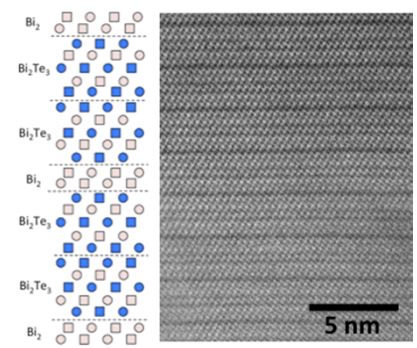
Dramatic reduction in low-temperature thermal conductivity



P. Sharma, et al. PRB 83 (2011) 235209.

Electron diffraction and HRSTEM show ordering in $(Bi_2)_m(Bi_2Te_3)_n$ series

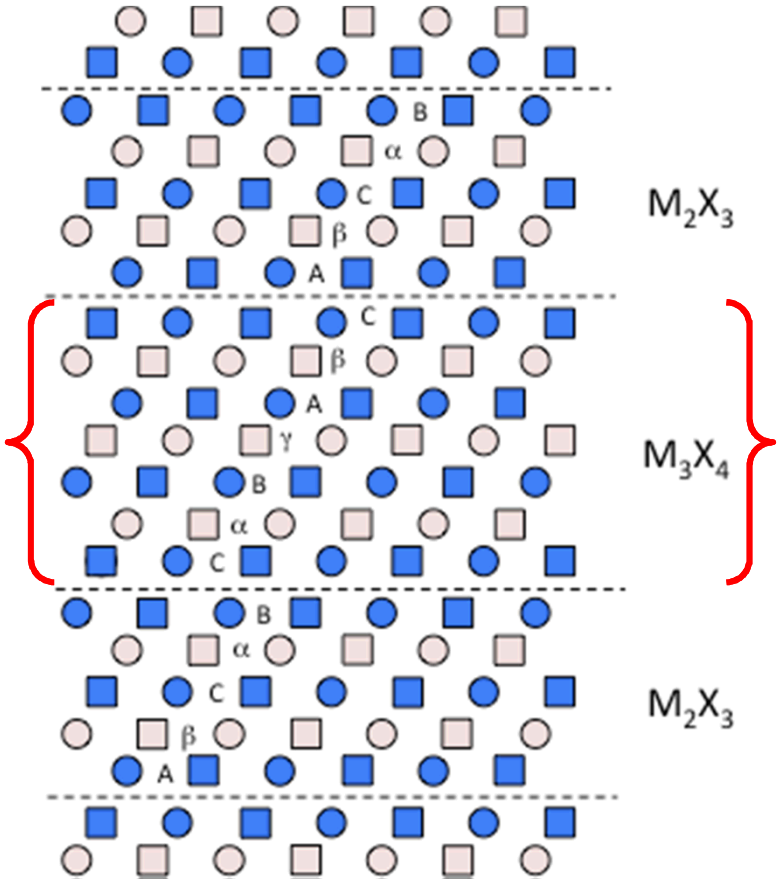




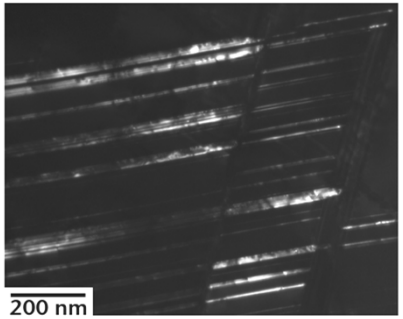
Medlin & Snyder, JOM 2013

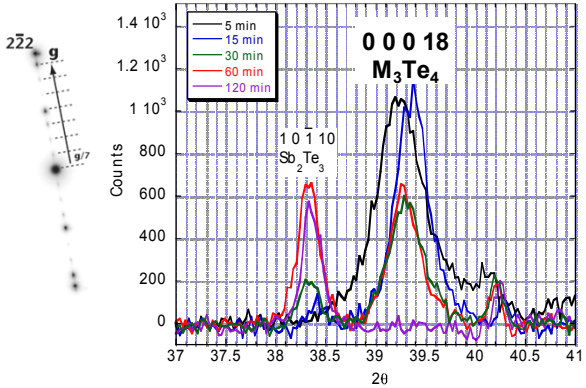
Layered structure allows flexibility in accommodating variations in composition

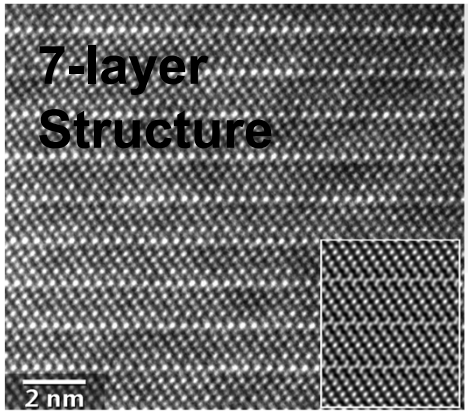
Metal rich, 7-Layer M_3X_4 fault

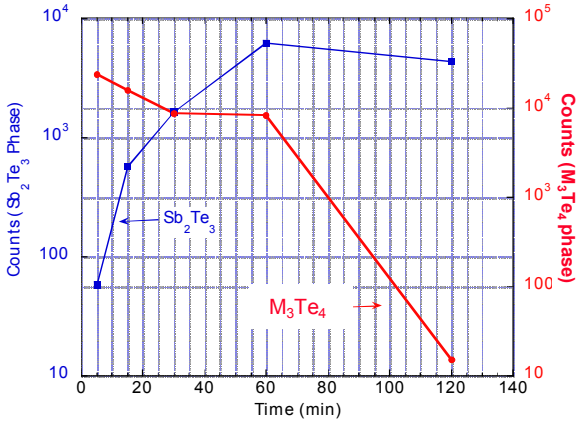


Example: $(Ag,Sb)_3Te_4$ transition phase during nucleation of Sb_2Te_3 precipitates in $AgSbTe_2$









Sharma, Sugar, & Medlin, Journal of Applied Physics (2010).
Sugar and Medlin, Journal of Materials Science (2011)

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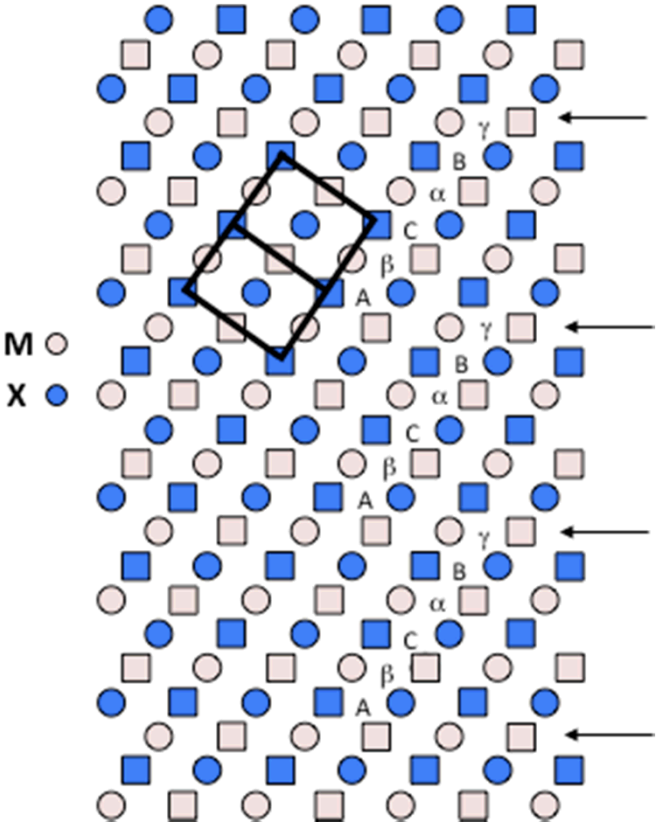
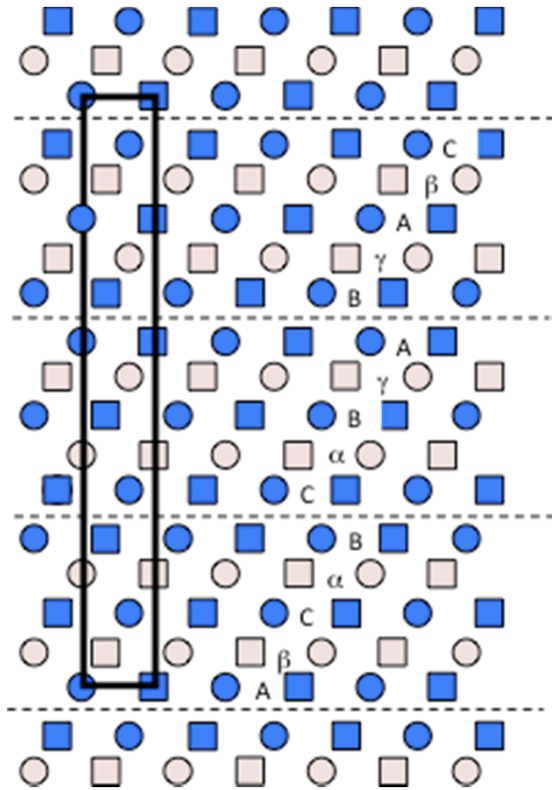
Tetradymite and Rocksalt structures are closely related

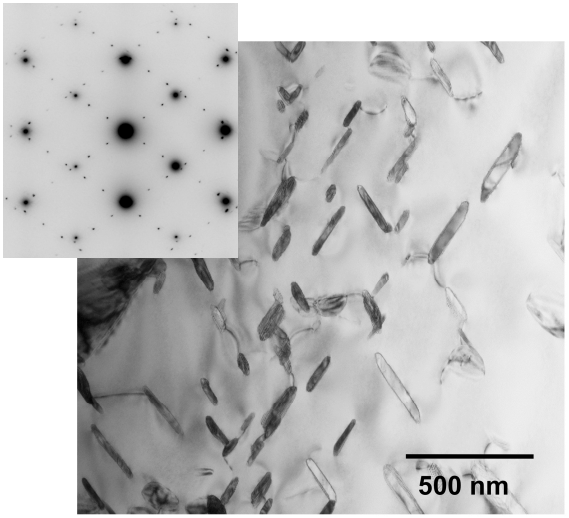
Rocksalt (MX) Structure



Tetradymite (M_2X_3) Structure



Example: Crystallographically Aligned Sb_2Te_3 precipitates in PbTe



Heinz, Snyder, Ikeda, and Medlin, Acta Mat. 2011

- Solid-state phase transformations in chalcogenides
- Structural interpretation of extended defects

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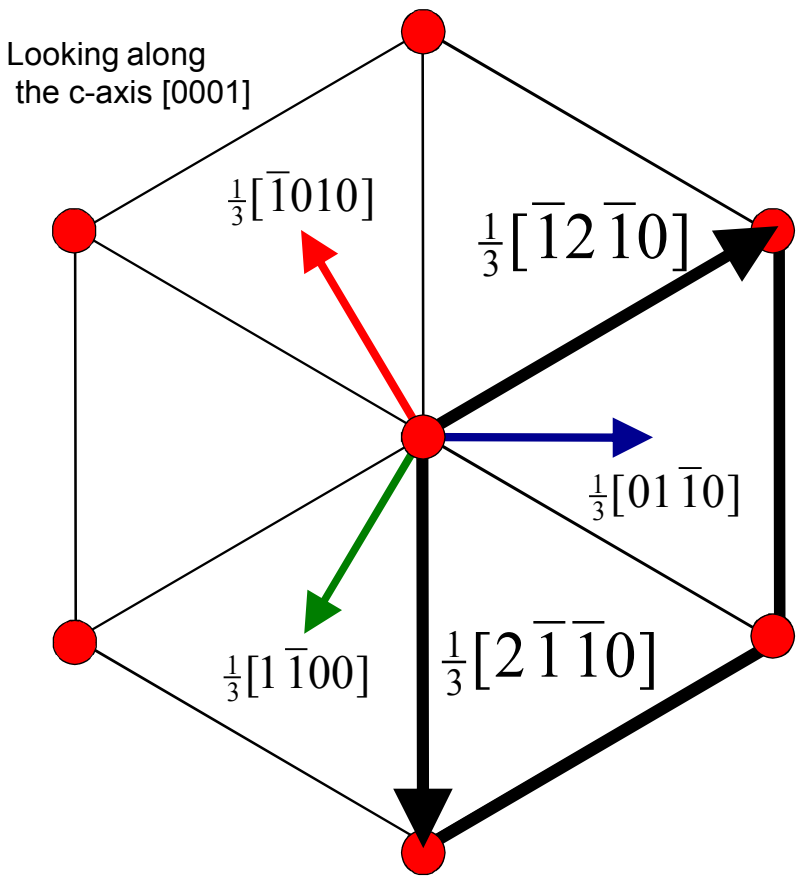
How do these structural considerations impact Dislocations and Interfaces?

Dislocations in Bismuth Telluride

Burgers vectors lying in basal plane



Array of 1/3<2-1-1 0> Dislocations in Bi_2Te_3

Fig. 1. Dislocation network in Bi_2Te_3. Note that certain segments of dislocations and certain node-points have left the foil

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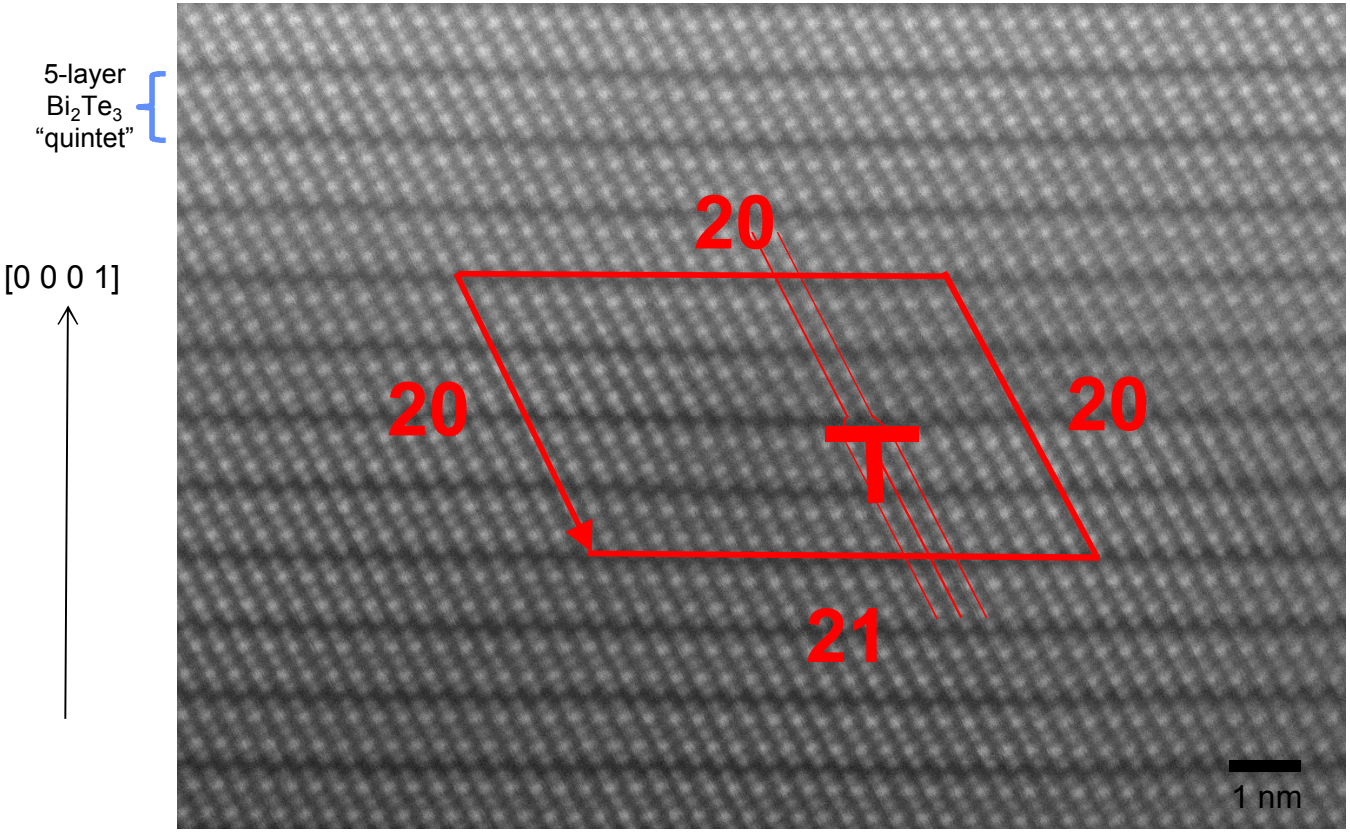
Dislocation Core structure: termination at $Te^{(1)}$-$Te^{(1)}$ layer, dissociation



b=1/3<2 -1 -1 0>

T 60° mixed dislocation

LLNL-Titan
HAADF-STEM
300 keV

<2 -1 -1 0 > projection

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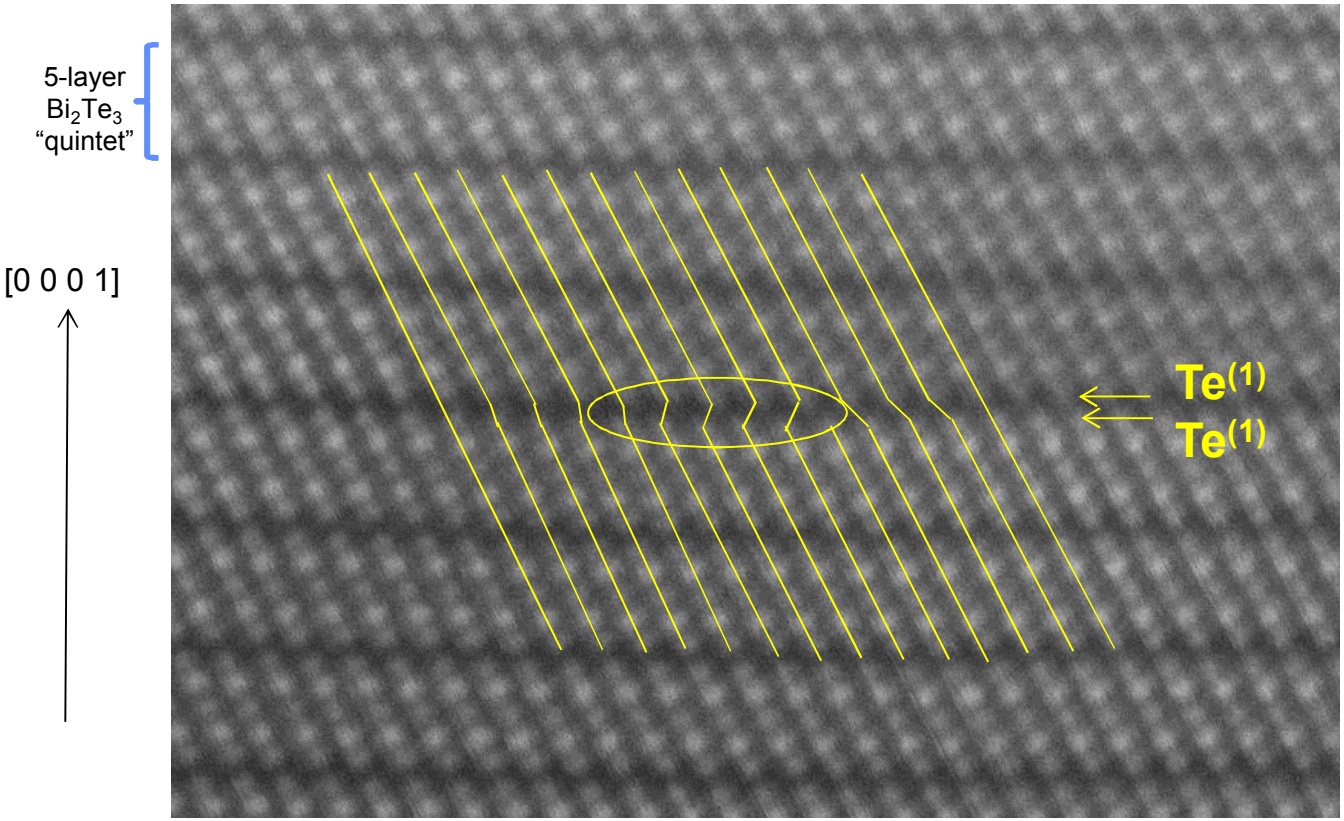
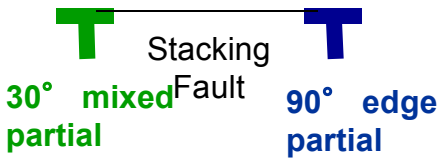
Dislocation Core structure: termination at $Te^{(1)}$-$Te^{(1)}$ layer, dissociation



b=1/3<2 -1 -1 0>

60° mixed dislocation



1/3<1 0 -1 0> partial dislocations.

LLNL-Titan HAADF-STEM 300 keV

Weak, van der Waals bonding likely favors dissociated dislocation core at $Te^{(1)}$-$Te^{(1)}$ layer

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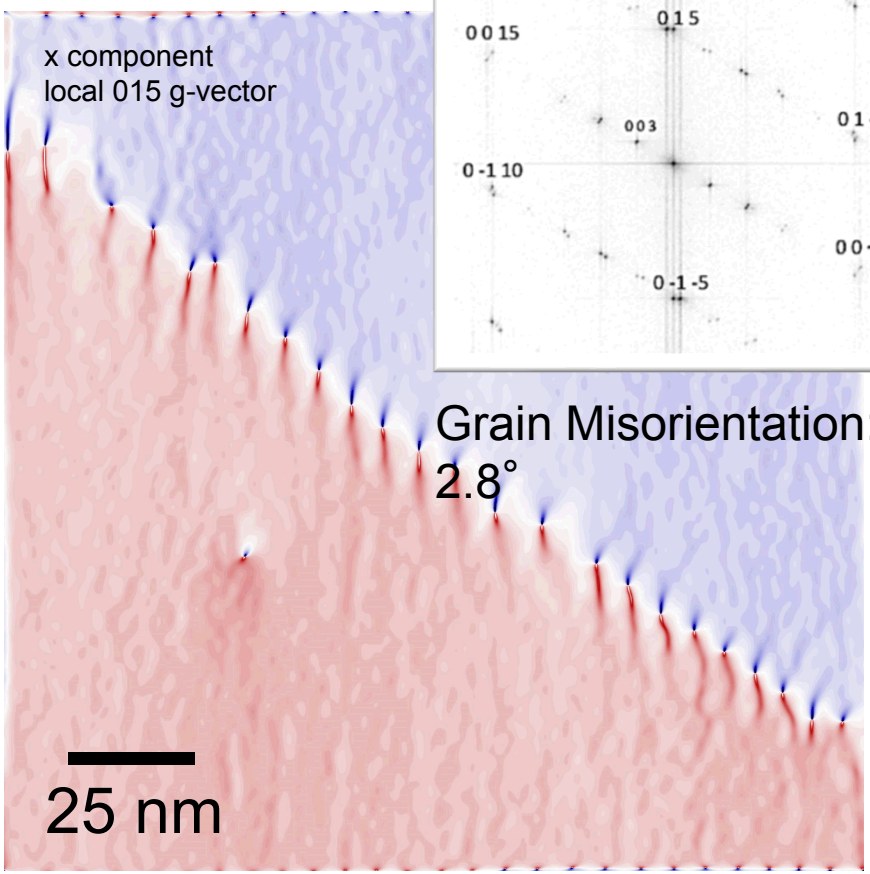
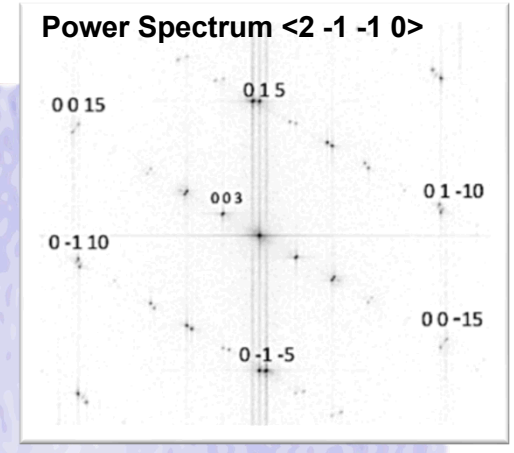
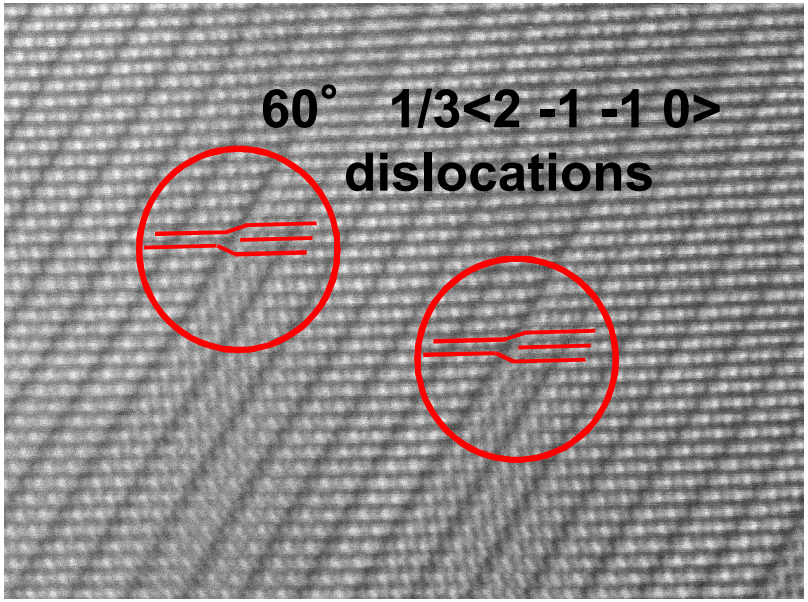
Grain Boundaries

Example: A Low Angle Tilt Boundary in Bi_2Te_3



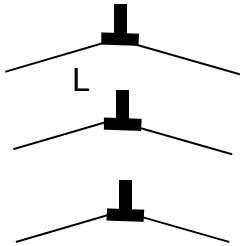


Grain Misorientation:
2.8°



Calculate tilt rotation from dislocation density

$$\theta = 2\sin^{-1}\left(\frac{b_{edge}}{2L}\right)$$



= 2.7° (calculated)
(2.8° measured)

L_{avg} = 8.0 nm

b_{edge} = 0.379 nm
(60° 1/3<2-1-10>
b=0.438 nm))

(for array of 60° dislocations, to be pure tilt, screw components must cancel)

HRSTEM
Analyzed using MacTempas Software
Geometric phase object routines:
Hÿtch,Snoek, Kilaas, Ultramicroscopy 1998

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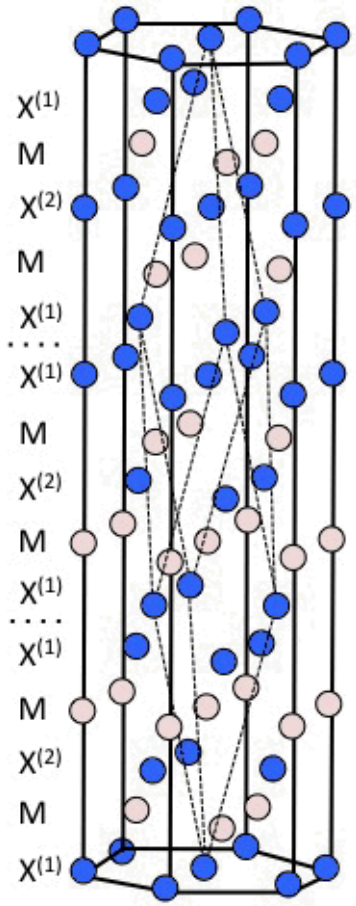
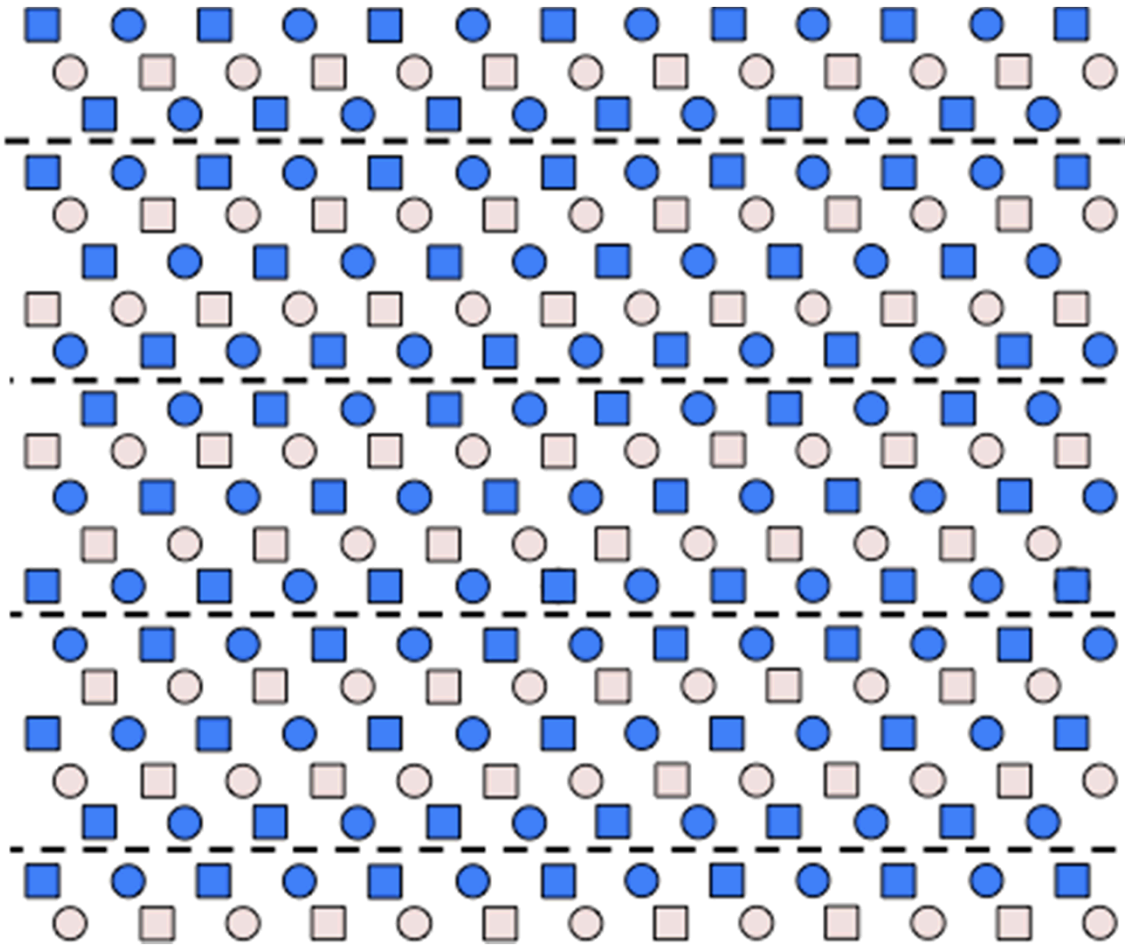
Non-basal dislocations: What happens if we pull out a quintuple unit?





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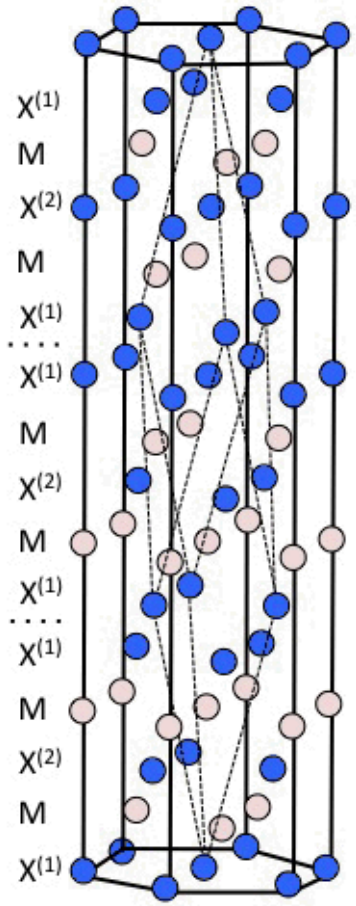
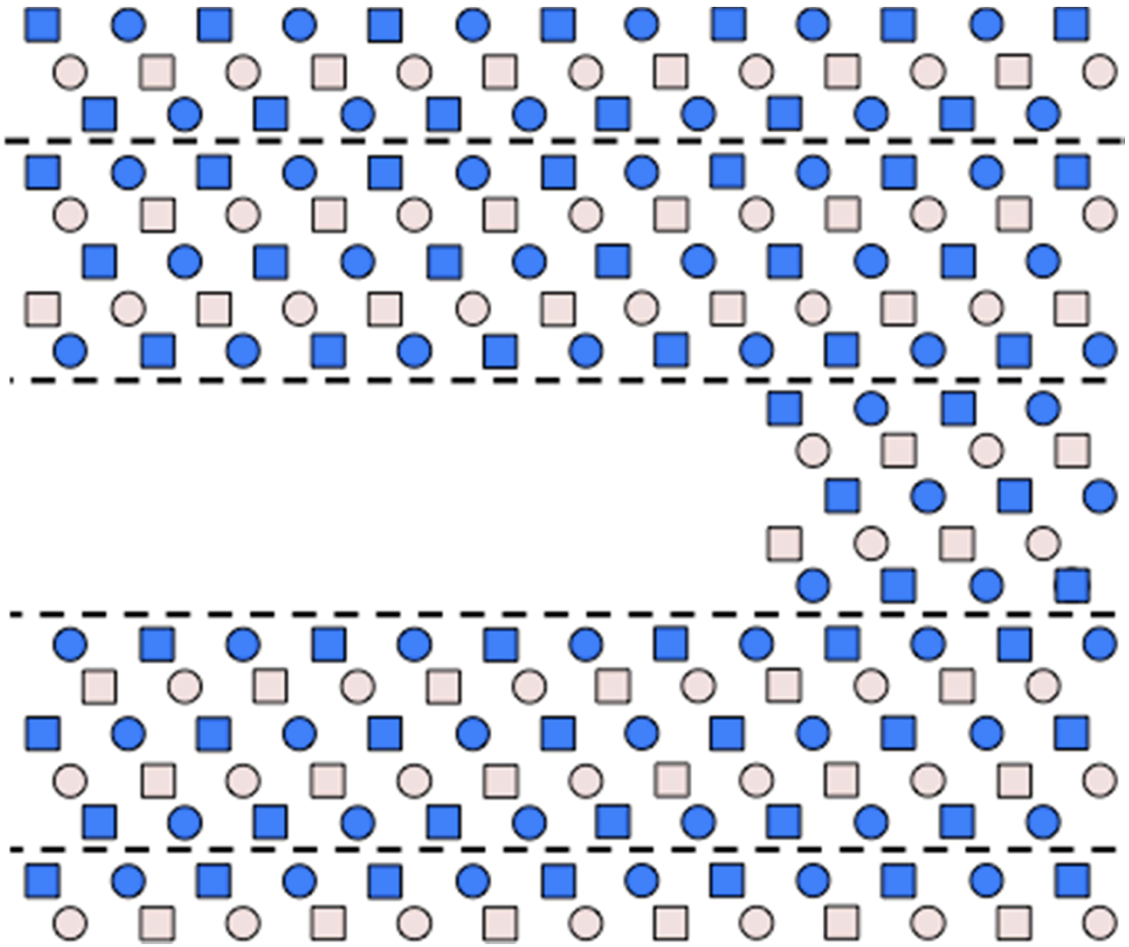
Non-basal dislocations:
What happens if we pull out a quintuple unit?





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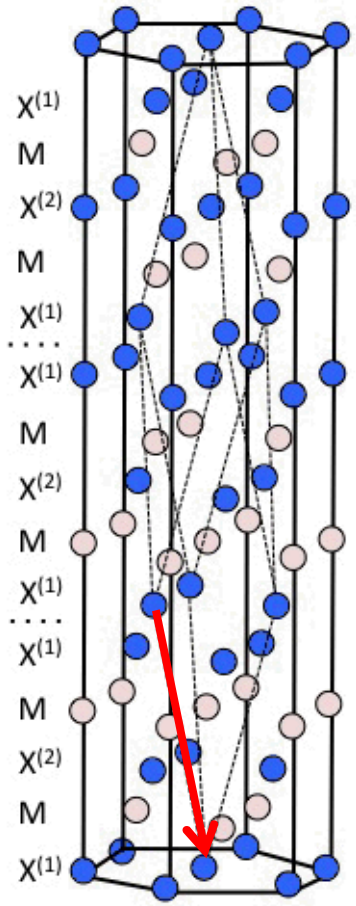
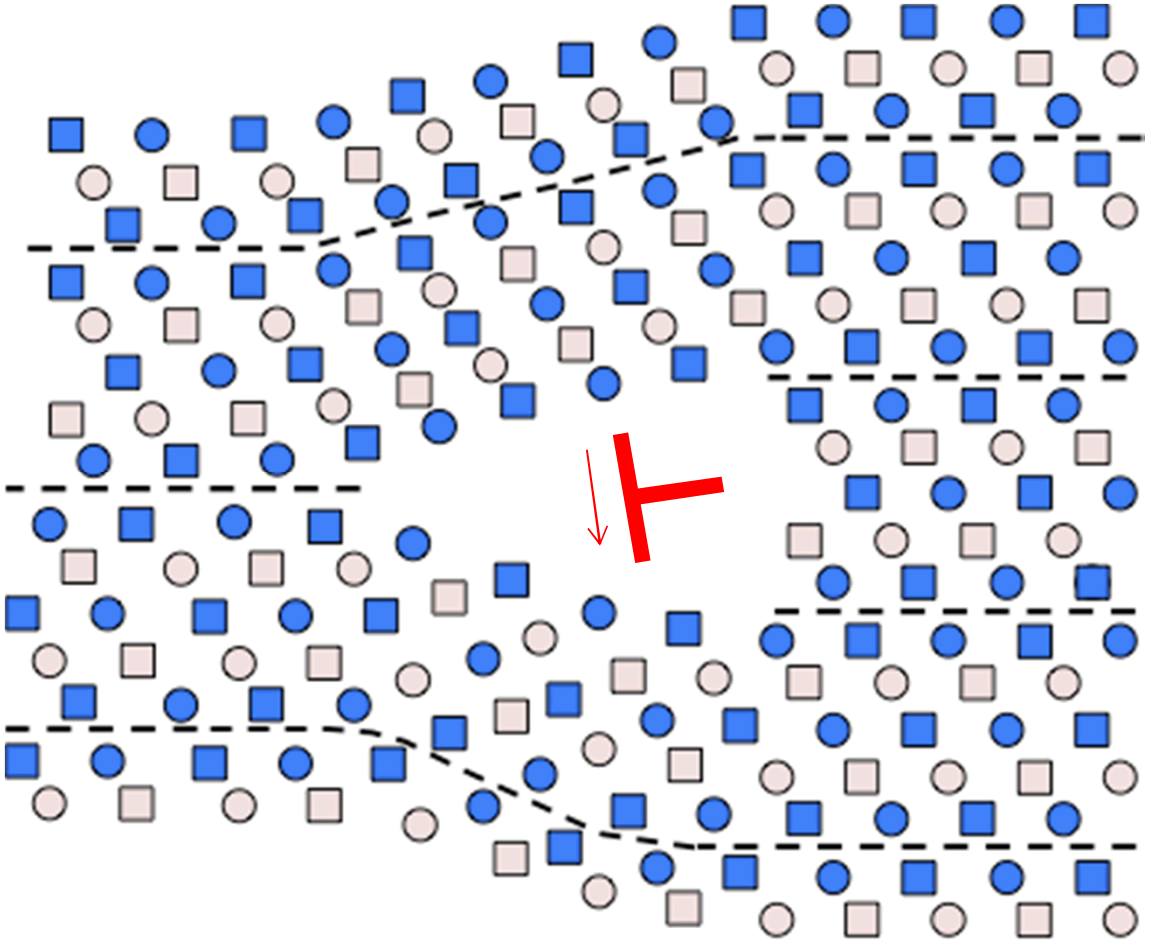
Non-basal dislocations: What happens if we pull out a quintuple unit?





$b = (1/3)[01\text{-}1\text{-}1)_H = [00\text{-}1]_R$

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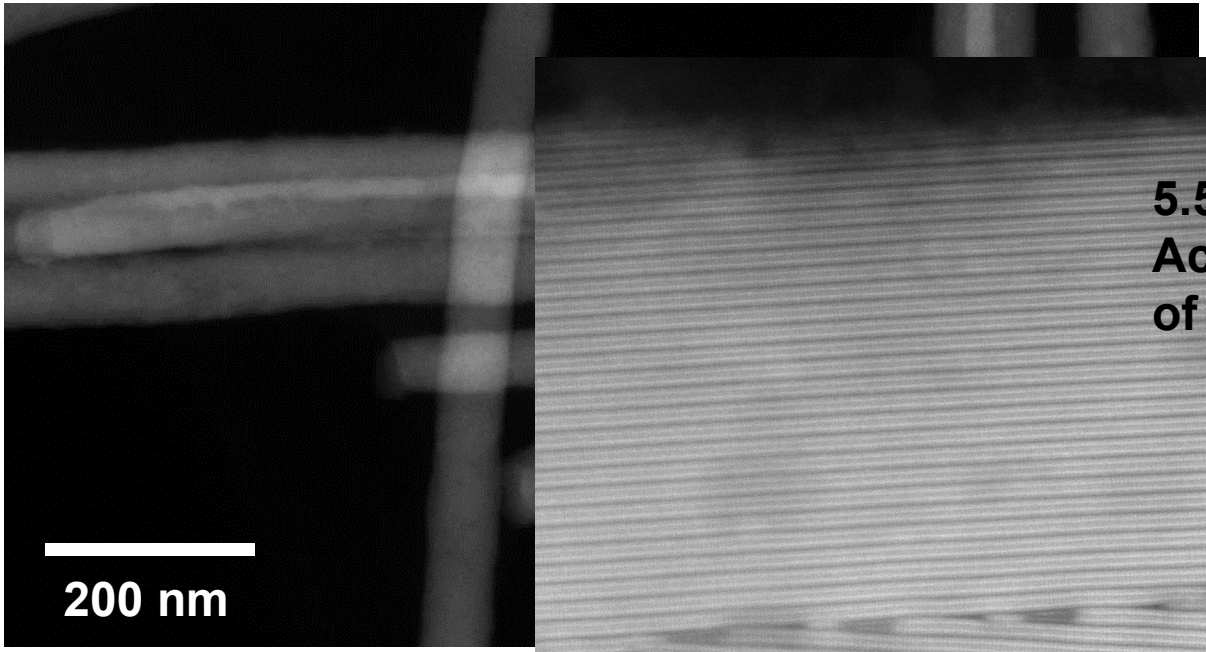
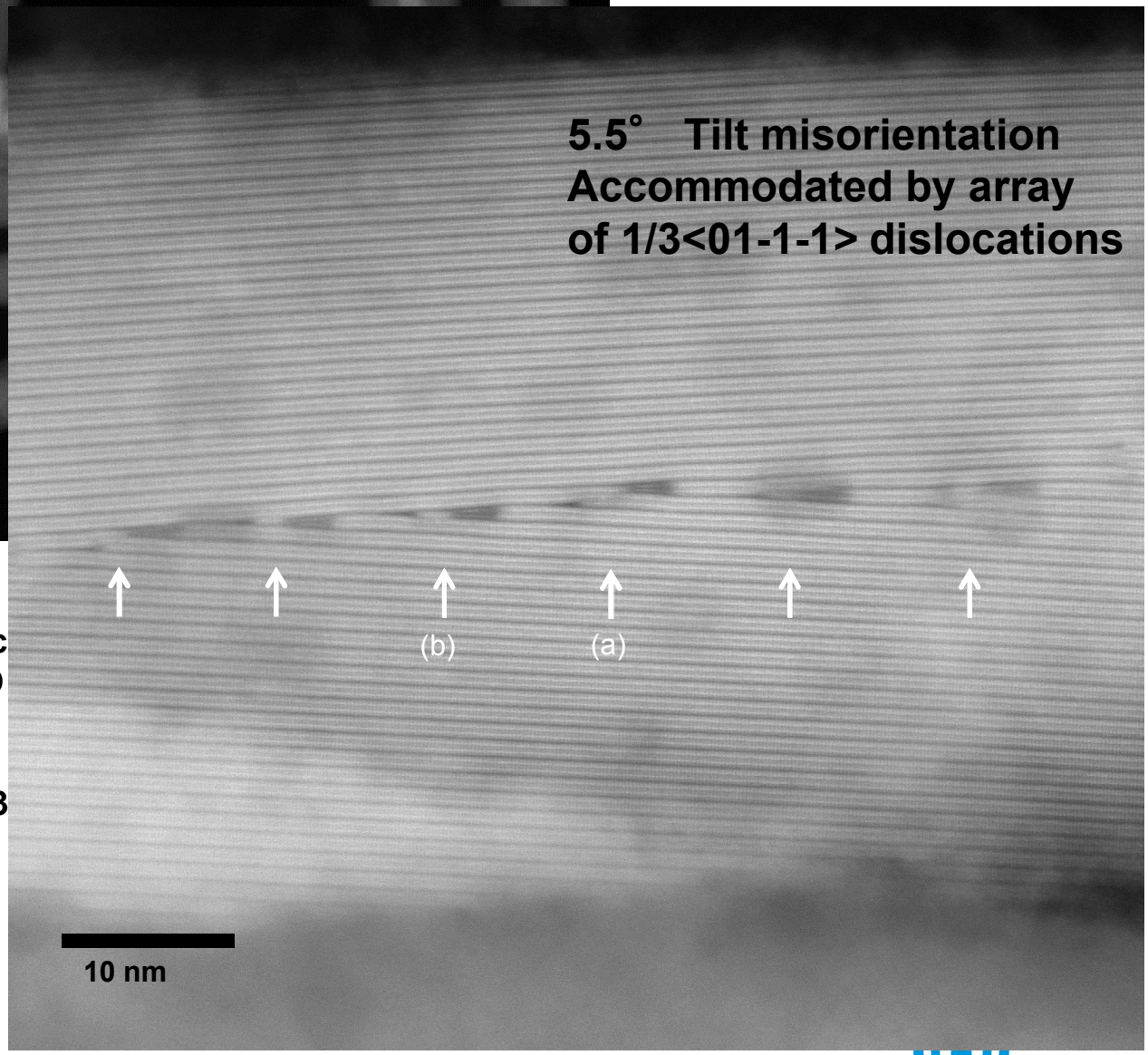
Dislocations in Bi_2Te_3 Nanowires





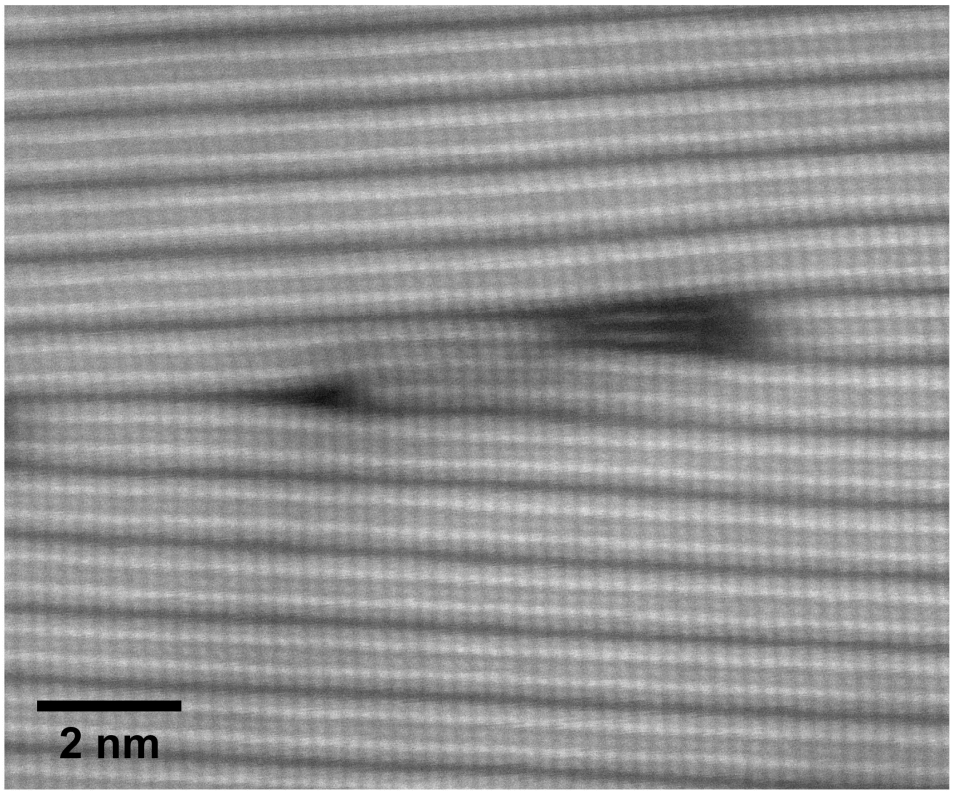
Wires formed by electrochemic deposition in nanoporous AAO templates.

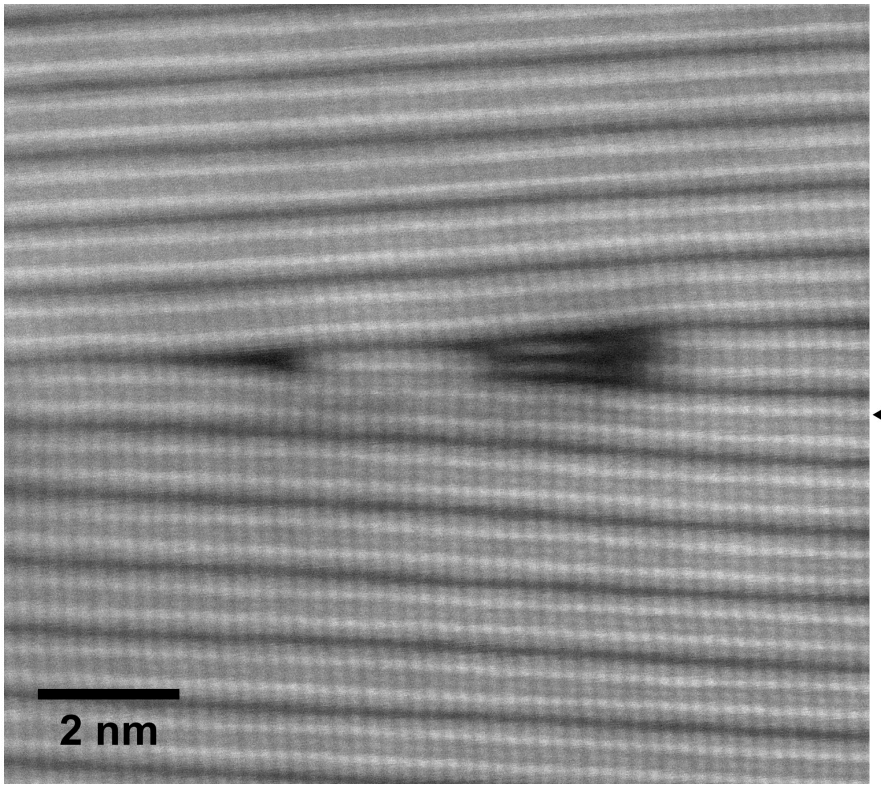
Free standing wires annealed 3 minutes at 300° C in Ar-3%H_2.

Medlin, Erickson, Limmer, Yelton, Siegal, J. Mat. Sci. 2014

Laboratories

Dislocations have dissociated core: two configurations





<1 0 -1 0> Projection

Medlin, Erickson, Limmer, Yelton, Siegal, J. Mat. Sci. 2014

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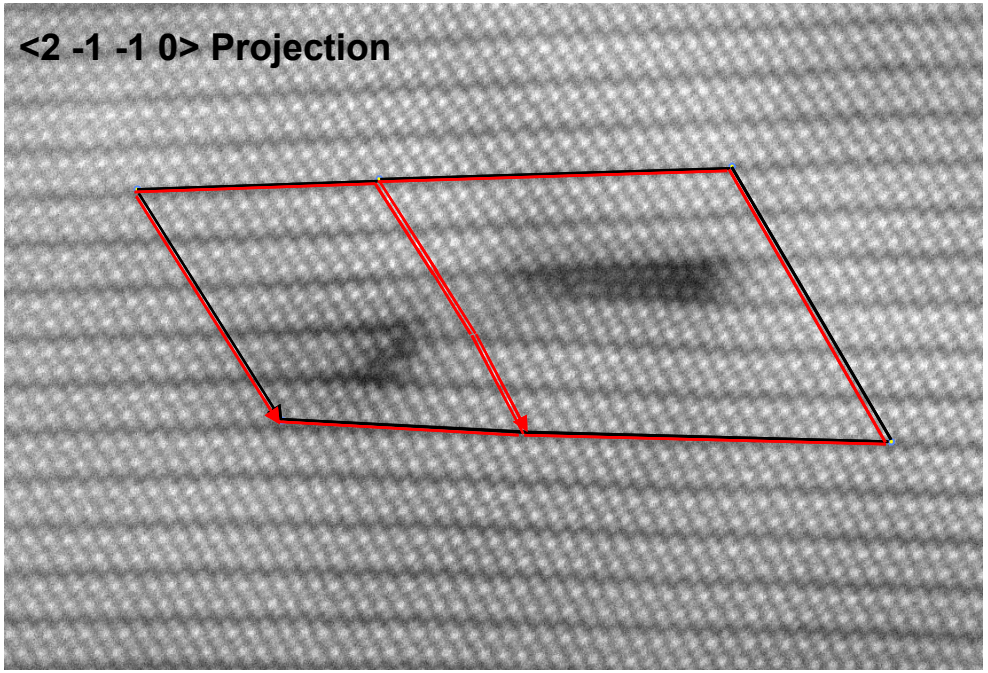
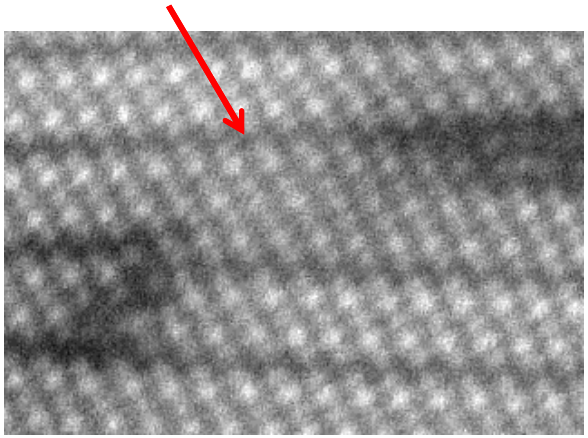
(1/3)[0 1 -1 -1] Dislocation in Bi_2Te_3:



Core structure:
Bi_3Te_4 7-layer fault



b = (1/3) [0 1 -1 -1] → (1/15) [0 5 -5 -2] + (3/15) [0 0 0 -1]

$b^2 > b_1^2 + b_2^2$

$109.8\ Å^2 > 22.9\ Å^2 + 37.2\ Å^2 = 60.2\ Å^2$

Reduced strain energy with dissociation

Medlin, Erickson, Limmer, Yelton, Siegal, J. Mat. Sci. 2014

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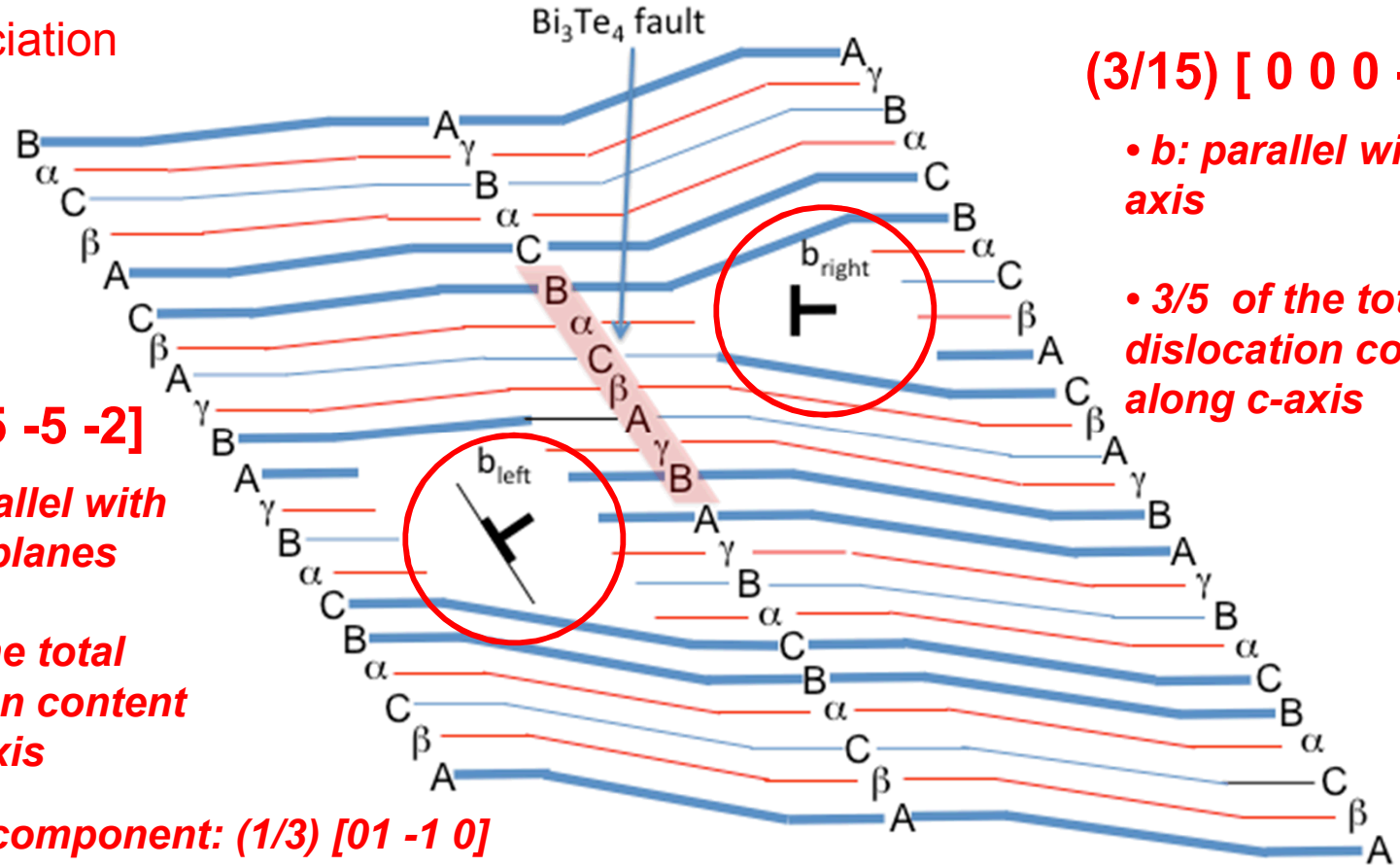
7-Layer Bi_3Te_4 faults: Mechanism to accommodate Te loss during annealing

Climb dissociation



(3/15) [0 0 0 -1]

- ***b: parallel with c-axis***
- ***3/5 of the total dislocation content along c-axis***

(1/15) [0 5 -5 -2]

- ***b is parallel with (0 1 -1 5) planes***
- ***2/5 of the total dislocation content along c-axis***

Horizontal component: (1/3) [01 -1 0]

- ***analogous to Shockley partial.***
- ***avoids fault in stacking resulting from additional 2 planes at Bi_3Te_4 fault***

Medlin, Erickson, Limmer, Yelton, Siegal, J. Mat. Sci. 2014

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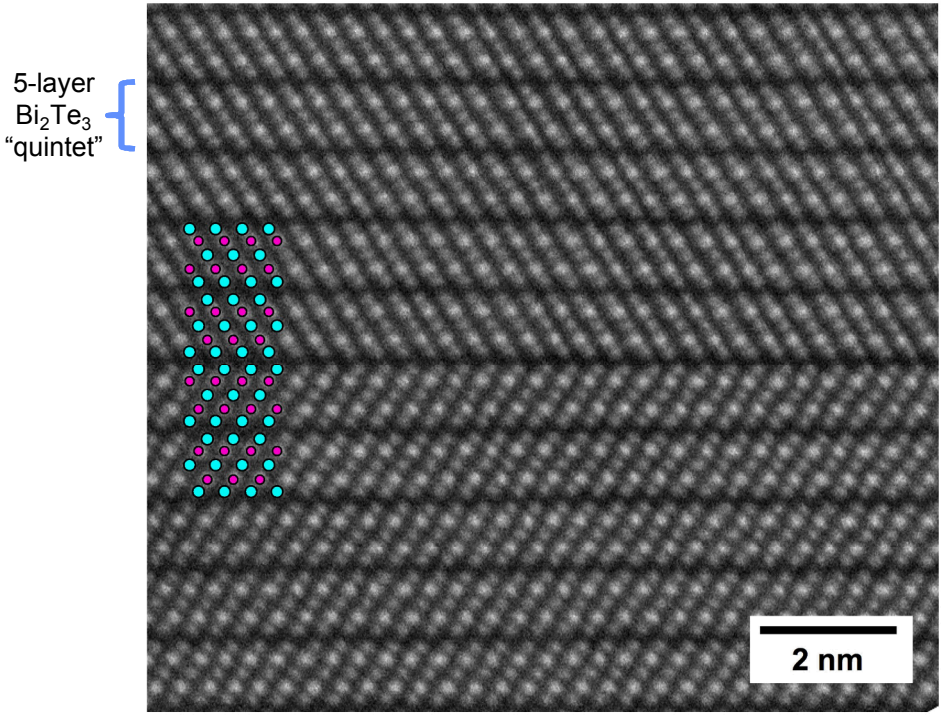
Atomic Structure of the Bi_2Te_3 Basal Twin: Energetic preference for termination at $Te^{(1)}$ sites

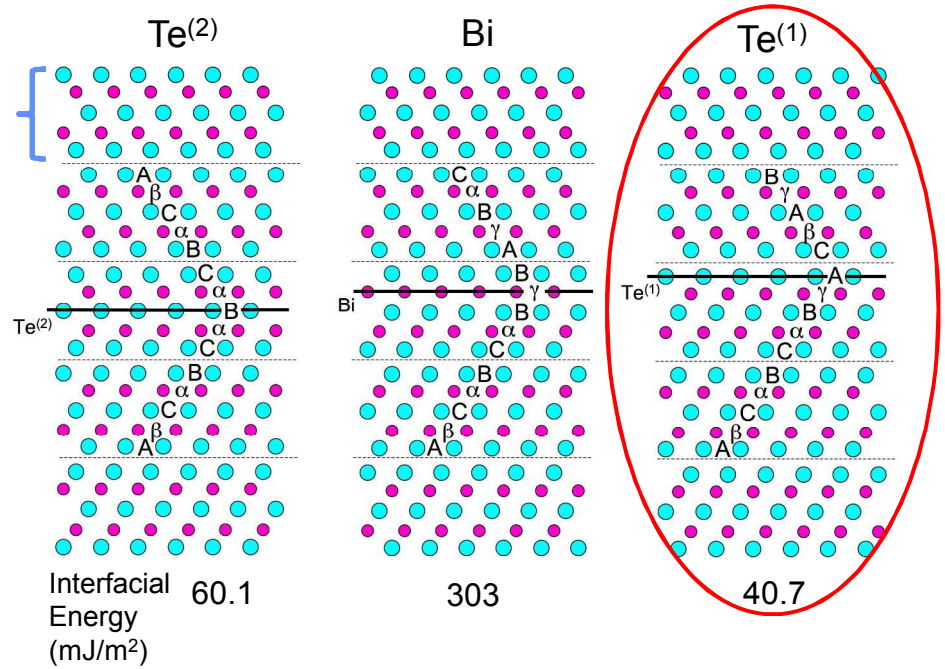
HAADF-STEM Imaging:

Twin Boundary Terminated at $Te^{(1)}$ layer



DFT Calculations:

Three Possible Compositional Terminations



Collaboration with LBNL *National Center for Electron Microscopy*
TEAM 0.5 Microscope

D.L. Medlin, Q.M. Ramasse, C. D. Spataru, N.C. Yang, J. Appl. Phys. (2010)

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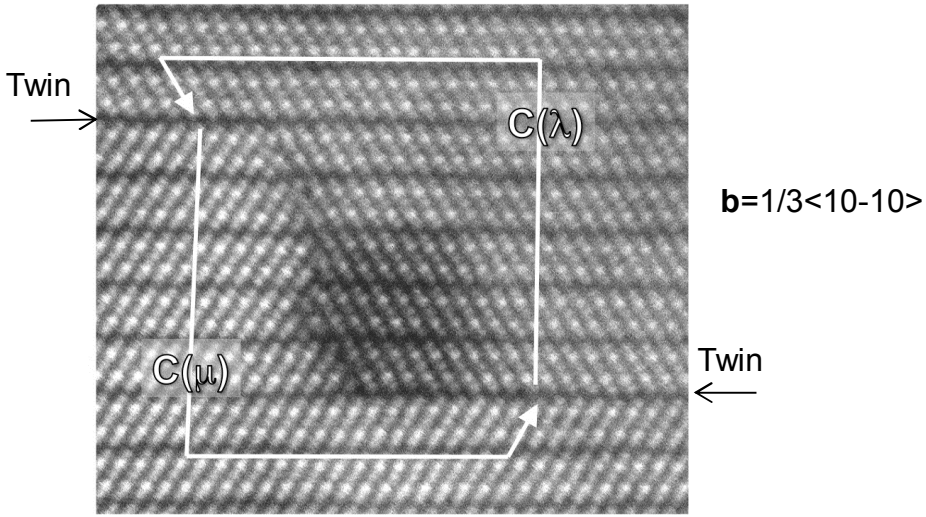
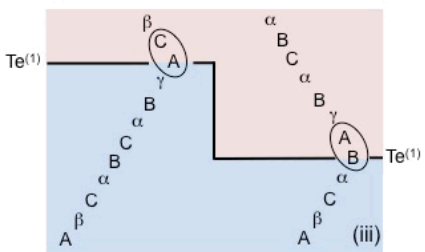
Preferential termination at $Te^{(1)}$ layers: Impact on boundary morphology

Example: step in Bi_2Te_3 Basal Twin:
25 planes high (5 quintets)



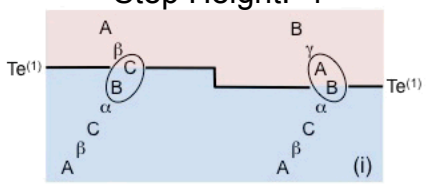
b=1/3<10-10>

Step Height: 5

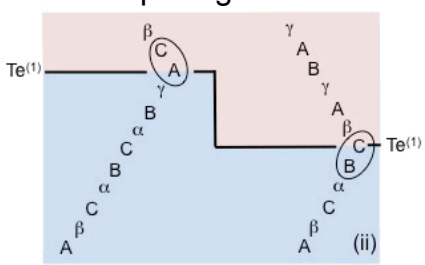


b=1/3<10-10>

Step Height: 1

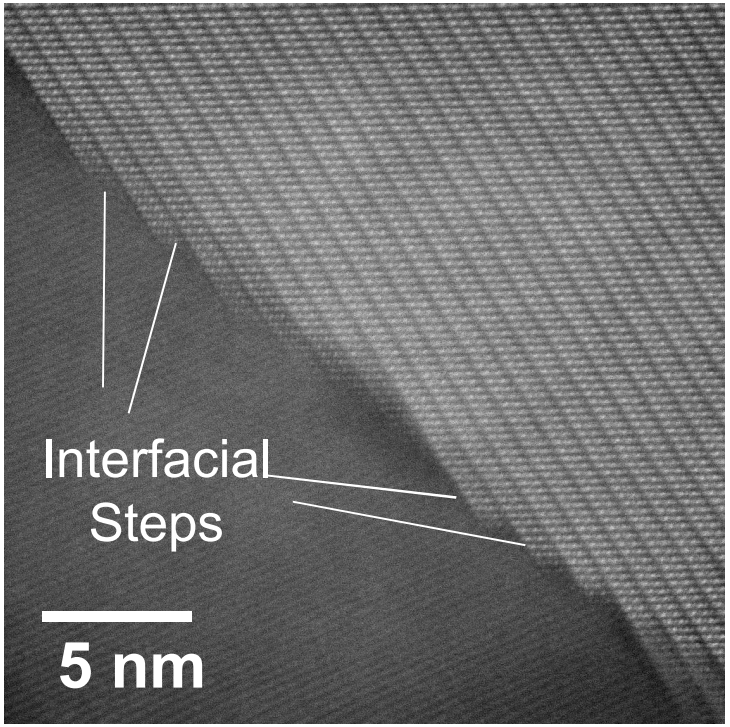


Step Height: 4



Medlin and Yang, Journal of Electronic Materials, (2012)

Grain boundary vicinal to (0001):
Steps of integral 5-plane Bi_2Te_3 Quintets



Medlin and Snyder, JOM (2013)

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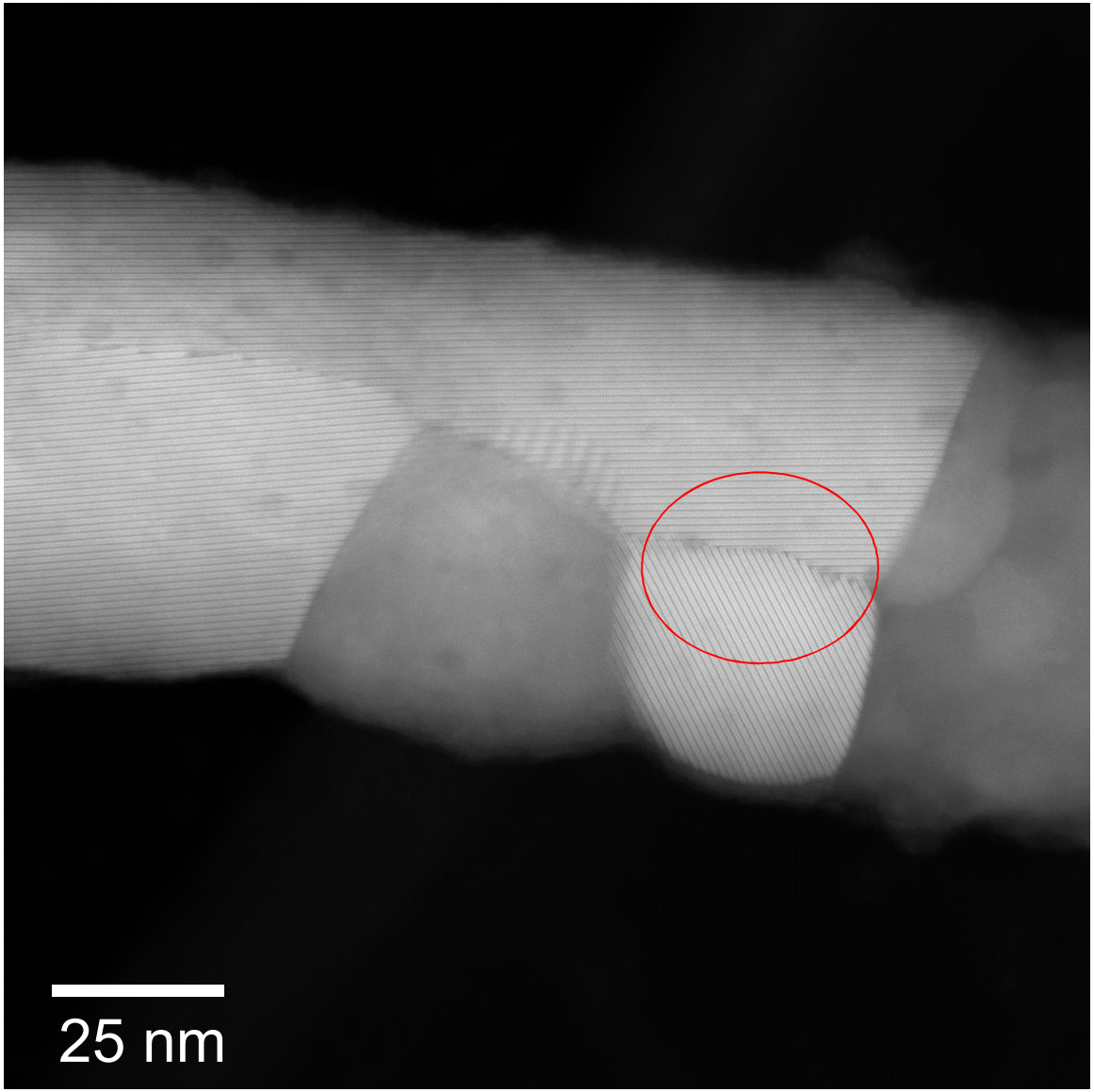
Bi_2Te_3 <2-1-1 0>//<-2 1 1 0> 63.78° Boundary

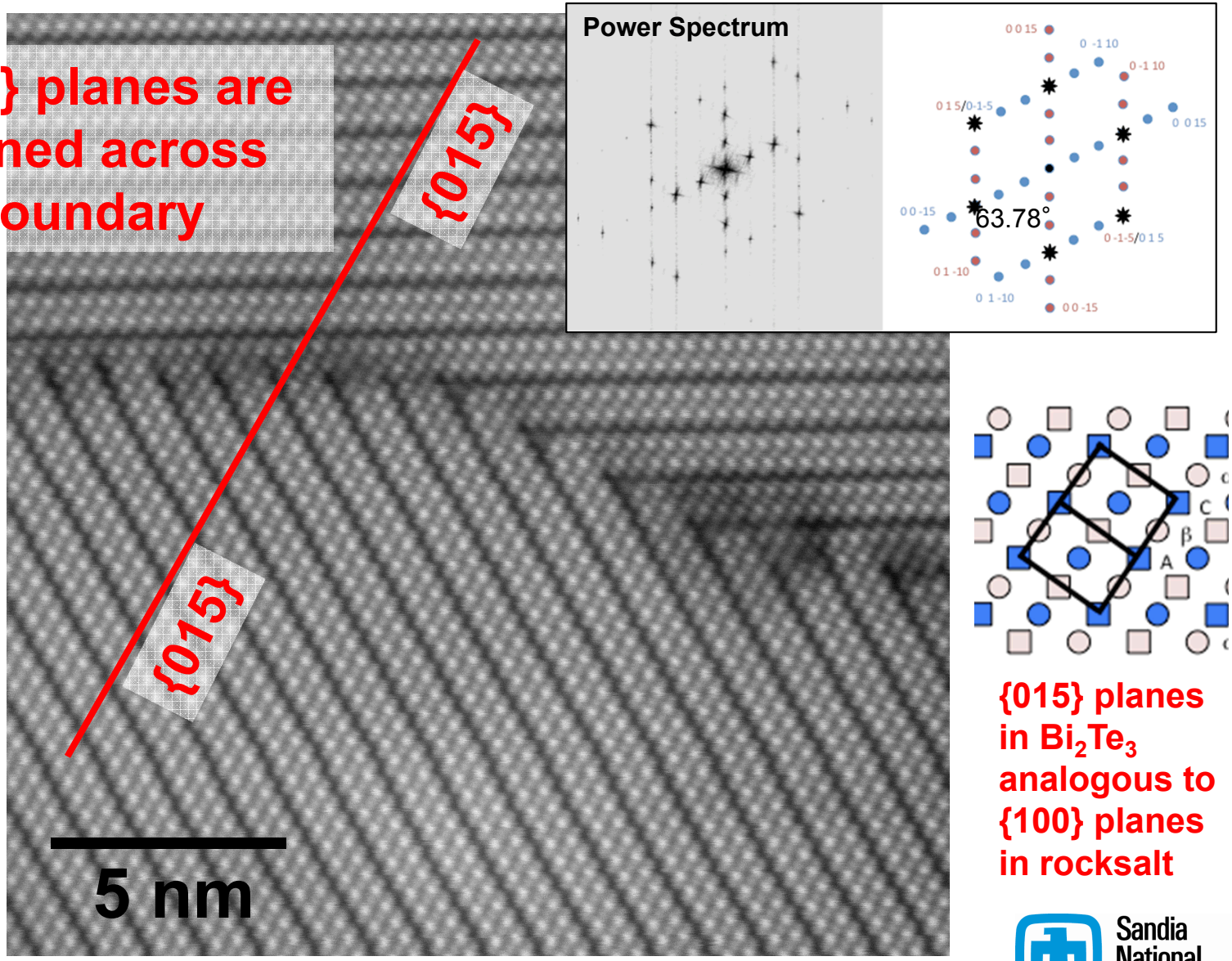
Electrodeposited
Bi_2Te_3 nanowire
Annealed 300° C



LLNL-Titan
HAADF-STEM
300 keV

Sandia National Laboratories

Bi_2Te_3 <2-1-1 0>//<-2 1 1 0> 63.78° Boundary



Electrodeposited Bi_2Te_3 nanowire
Annealed 300° C

{015} planes in Bi_2Te_3 analogous to {100} planes in rocksalt

LLNL-Titan
HAADF-STEM
300 keV

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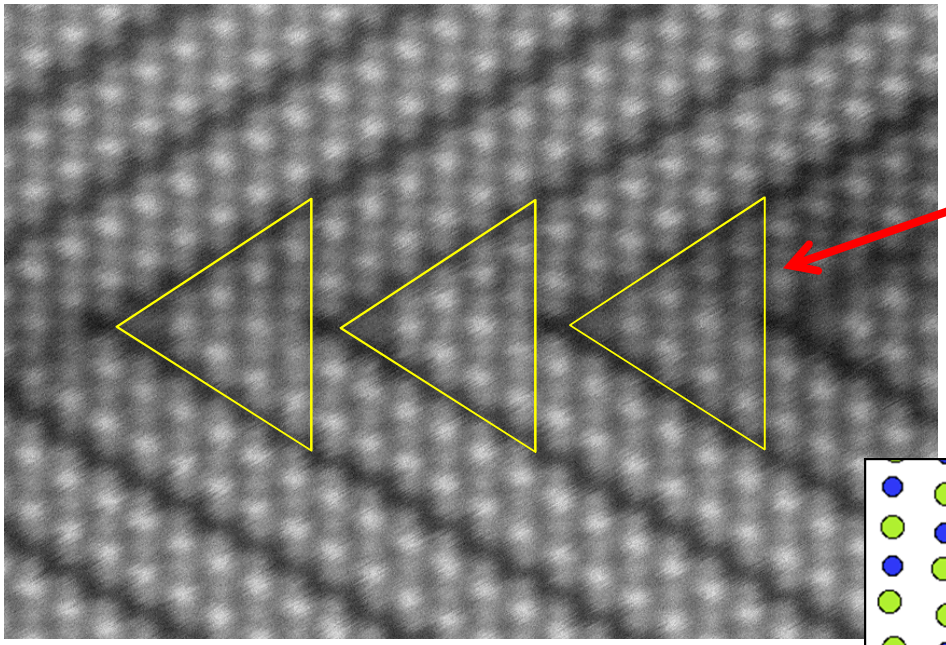
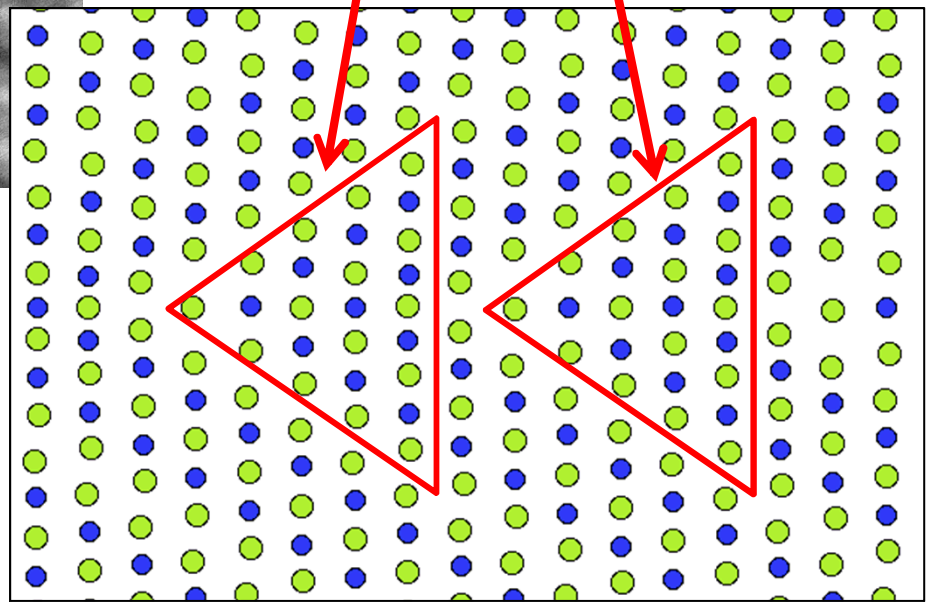
Symmetrical Interface Configuration

(0,-1,1,13) interface inclination



Rocksalt coordinated grain boundary units



Each triangular unit:

10 Bi 15 Te

2:3 ratio of Bi and Te maintained at interface

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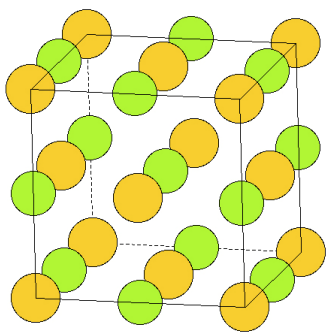
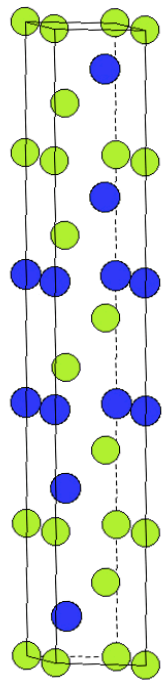
Heterophase Rocksalt/Tetradymite Telluride Interfaces

Rock-Salt
($PbTe$, $AgSbTe_2$)



Fm-3m

Tetradymite
(Bi_2Te_3,Sb_2Te_3)



R-3m

-Interest in forming thermoelectric nanocomposites of rock-salt and tetradymite tellurides:

-Possibility for well ordered interfaces.

-Transformations provide bulk route to synthesis.

Ikeda, et al., Chem Mater. 2007

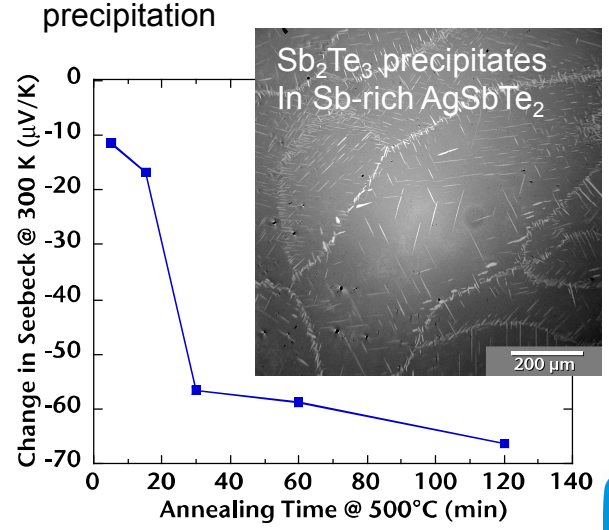
Snyder and Toberer, Nature Materials 2008

-$AgSbTe_2$:

-Constituent of TAGS $(GeTe)_x(AgSbTe_2)_{1-x}$ and LAST $(PbTe)_x(AgSbTe_2)_{1-x}$ zT ~ 1.8

-High performance TE material: zT > 1.2

-Degradation of Seebeck coefficient with Sb_2Te_3 precipitation



Sharma, Sugar, Medlin J. Appl. Phys. 2010

What happens at interface?
How do transformations occur?
Misfit accommodation?

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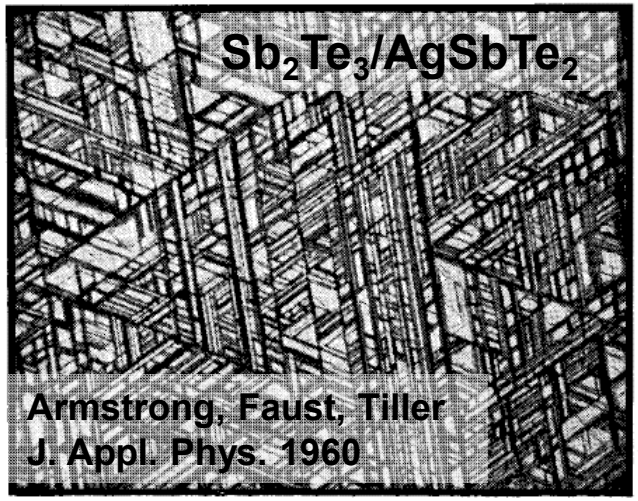
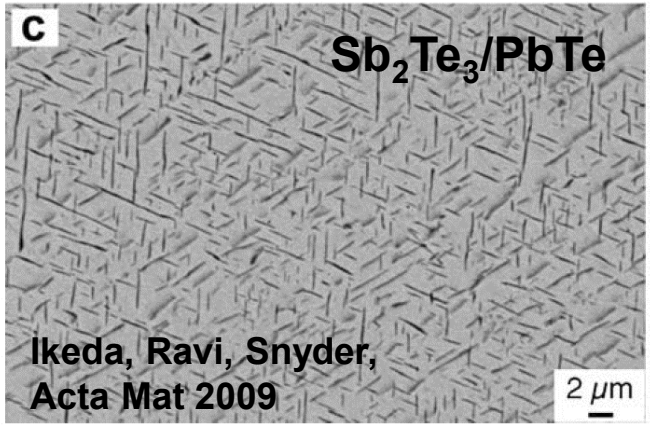
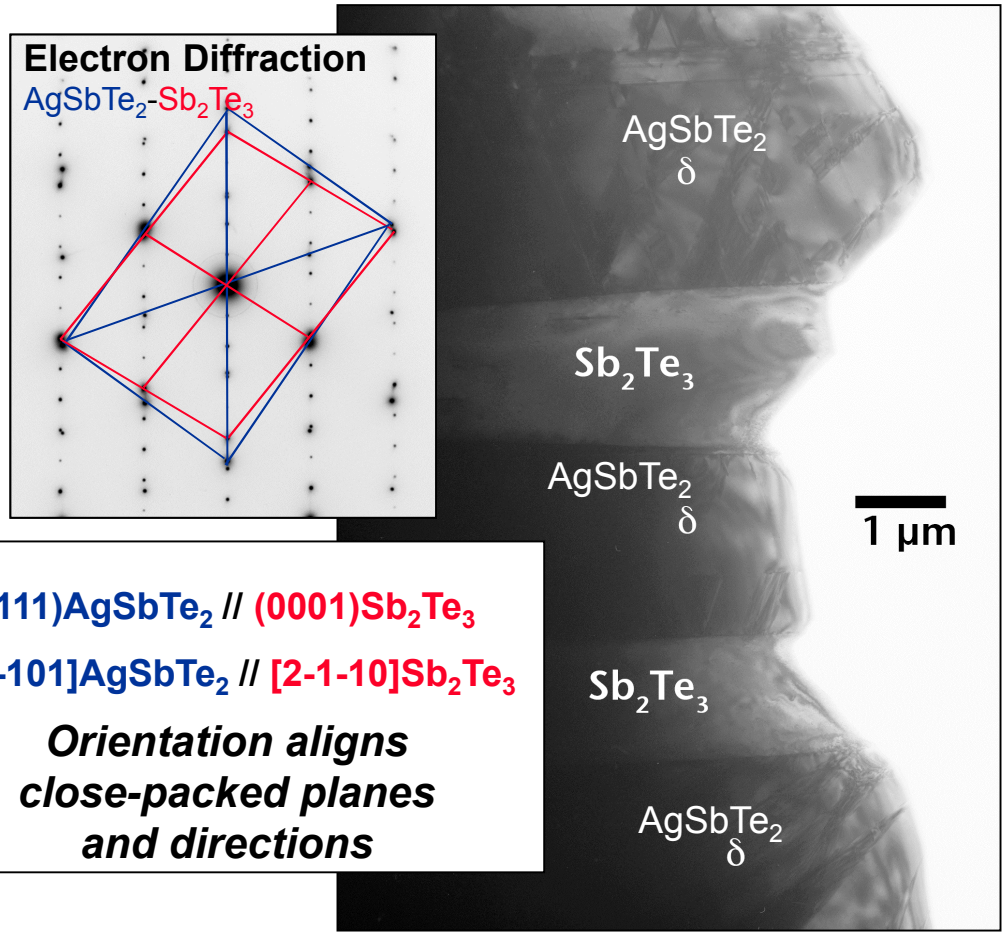
Crystallographic alignment between rocksalt and tetradymite phases

Widmanstätten plates





TEM $Sb_2Te_3/AgSbTe_2$



(111)$AgSbTe_2$ // (0001)Sb_2Te_3

[-101]$AgSbTe_2$ // [2-1-10]Sb_2Te_3

Orientation aligns close-packed planes and directions

Medlin and Sugar,
Scripta Mat 2010

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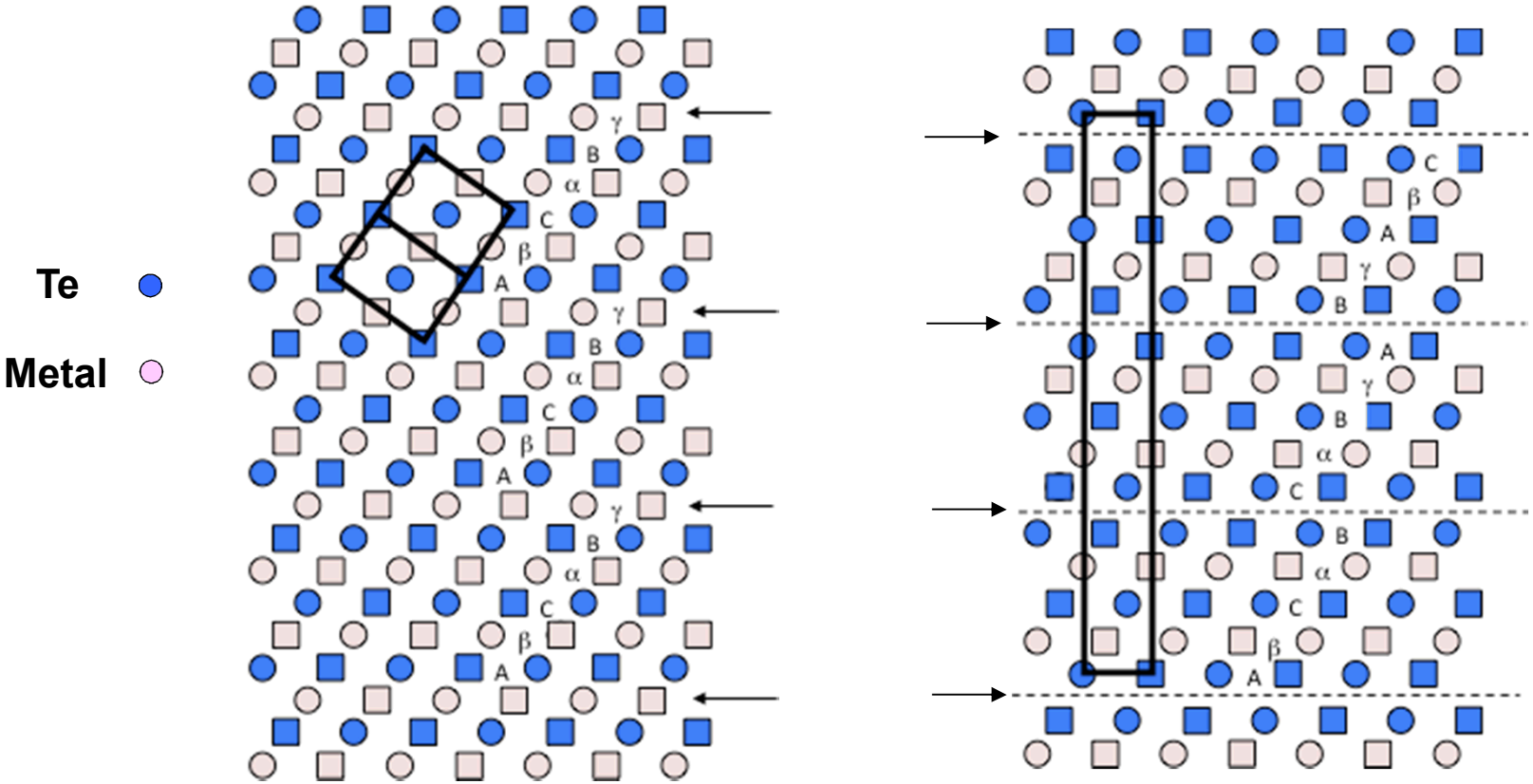
How to convert between the rocksalt and tetradymite structures?

Rocksalt

(MTe)

Tetradymite

(M_2Te_3)



-Remove metal plane every 6 layers

-Shear blocks by 1/3<10-10> (or 1/6<112> relative to cubic coordinates)

N. Frangis et al., J. Solid State Chemistry 84 (1990)

Transformation can be accomplished through a ledge mechanism

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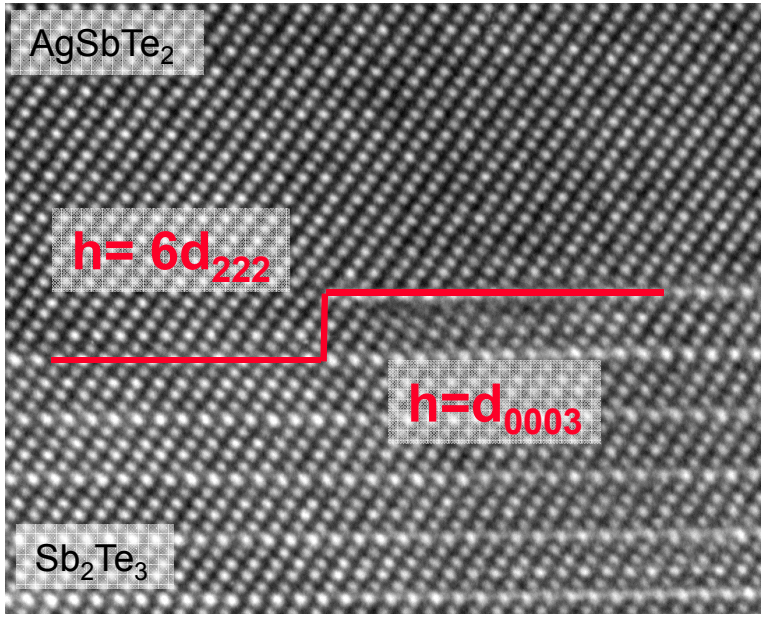
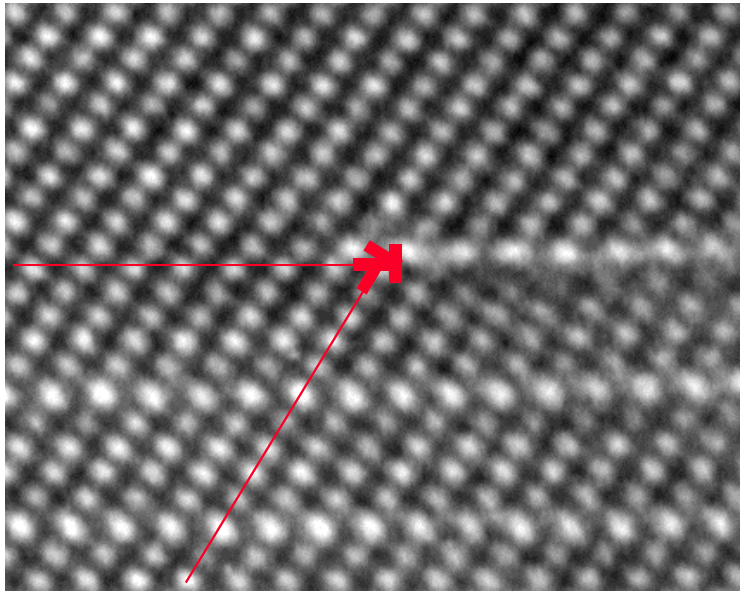
HRTEM : Step at $AgSbTe_2/Sb_2Te_3$ Interface





JEOL 4000EX HRTEM

Defect has both step and dislocation character.

-Interfacial "Disconnection" (e.g. Hirth and Pond, Acta Mat 1996).

-Geometric properties of disconnections control mass flux and structural rearrangements of phase transformations.

Step joins 6 {222} planes in $AgSbTe_2$ with 5 {000 15} planes in Sb_2Te_3

Complex dislocation configuration.

Medlin and Sugar, Scripta Materialia, 2010.

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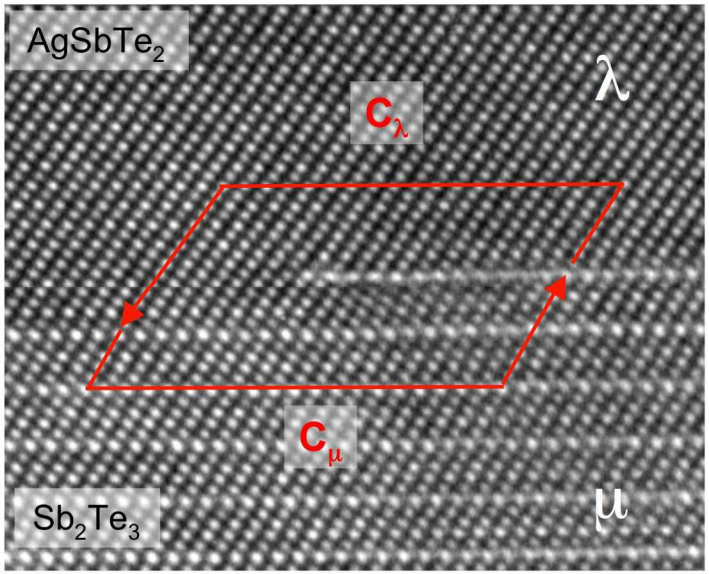
Role of defect in precipitate growth:

Burgers vector:



Upper crystal circuit

Lower crystal circuit

$$\mathbf{b} = -(\mathbf{C}_\lambda + \mathbf{P}\mathbf{C}_\mu)$$

-Coordinate Transformation From Tetradymite to Rock-salt.
-Coherently strained reference frame

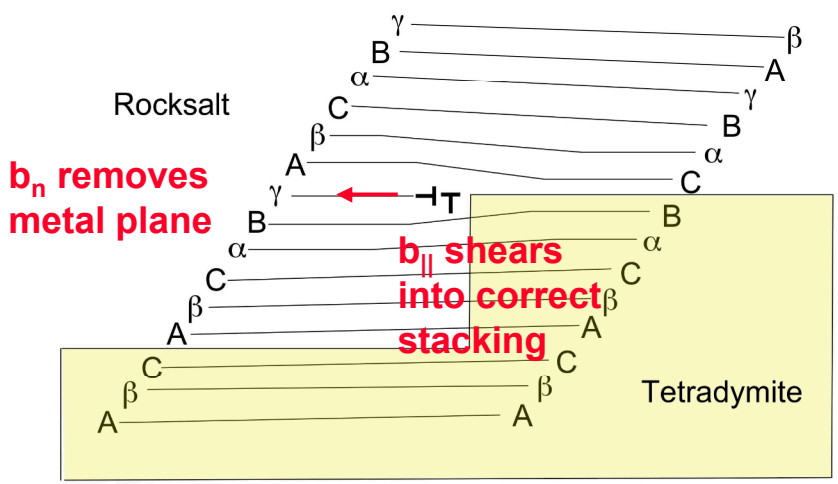
Resolve b into components normal and parallel to interface

$$\mathbf{b}_n = (a_{cub} - c_{hex}/3\sqrt{3})[111]$$

- *mismatch of step heights.*
- *$|b_n|$=0.3747Å*

$$\mathbf{b}_{\parallel} = \frac{a_{cub}}{6}[\bar{1}2\bar{1}]$$

- *Analogous to Shockley partial Dislocation*
- *$|b_{\parallel}|$=2.48Å*



Medlin and Sugar, Scripta Materialia, 2010.

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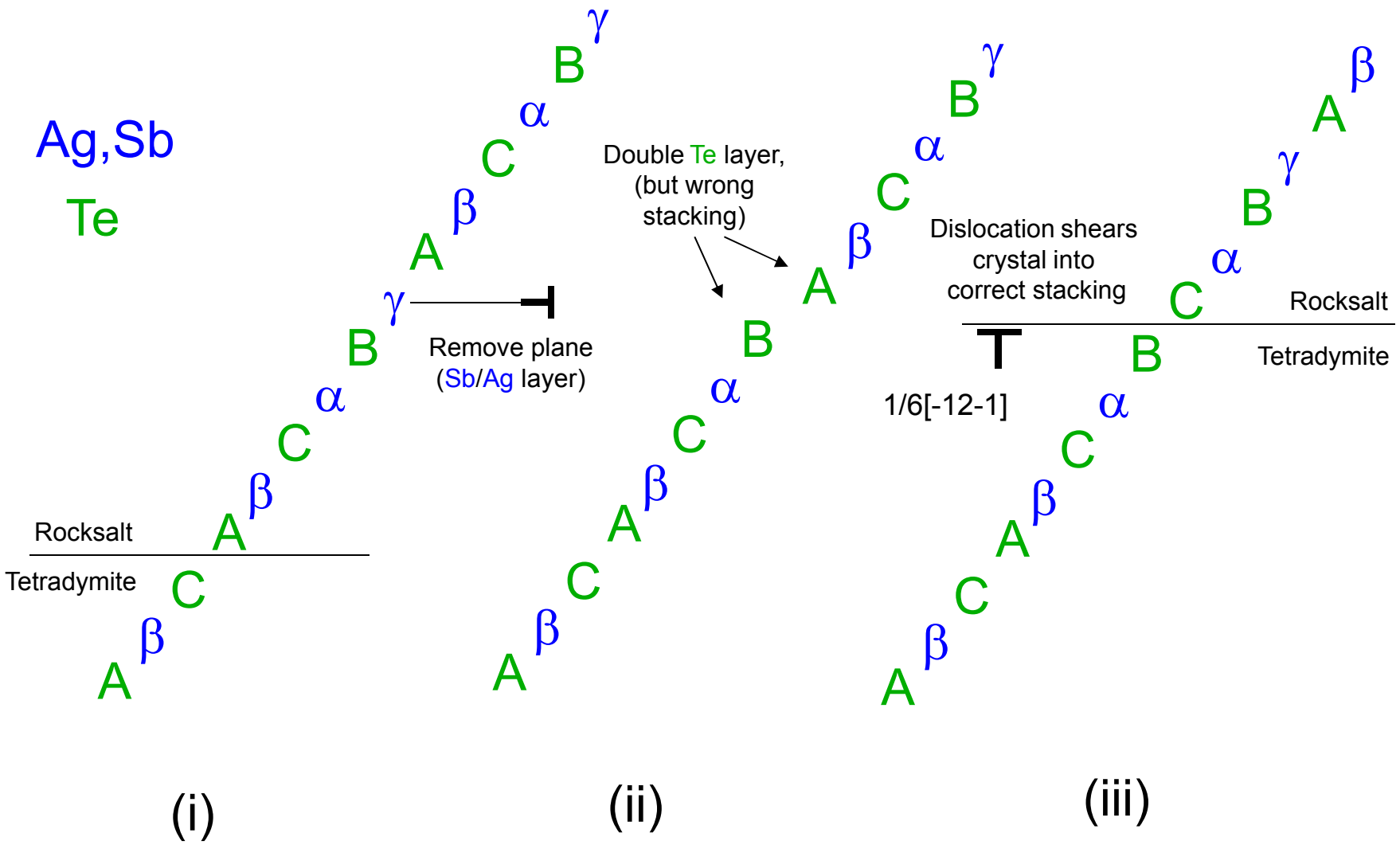
Schematic of Transformation Sequence



Medlin and Sugar, Scripta Materialia, 2010.

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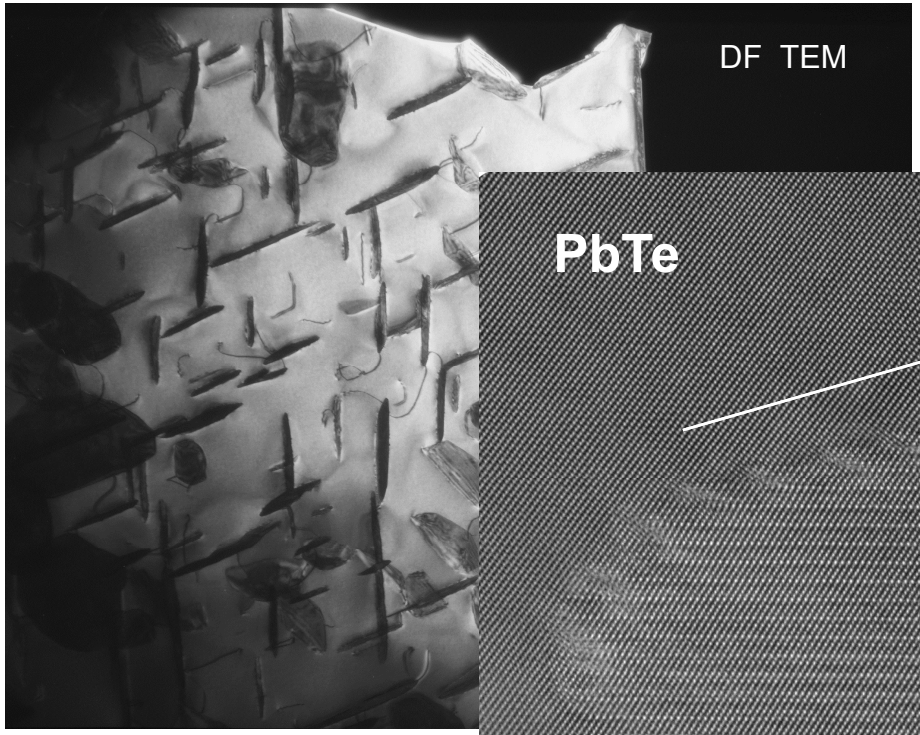
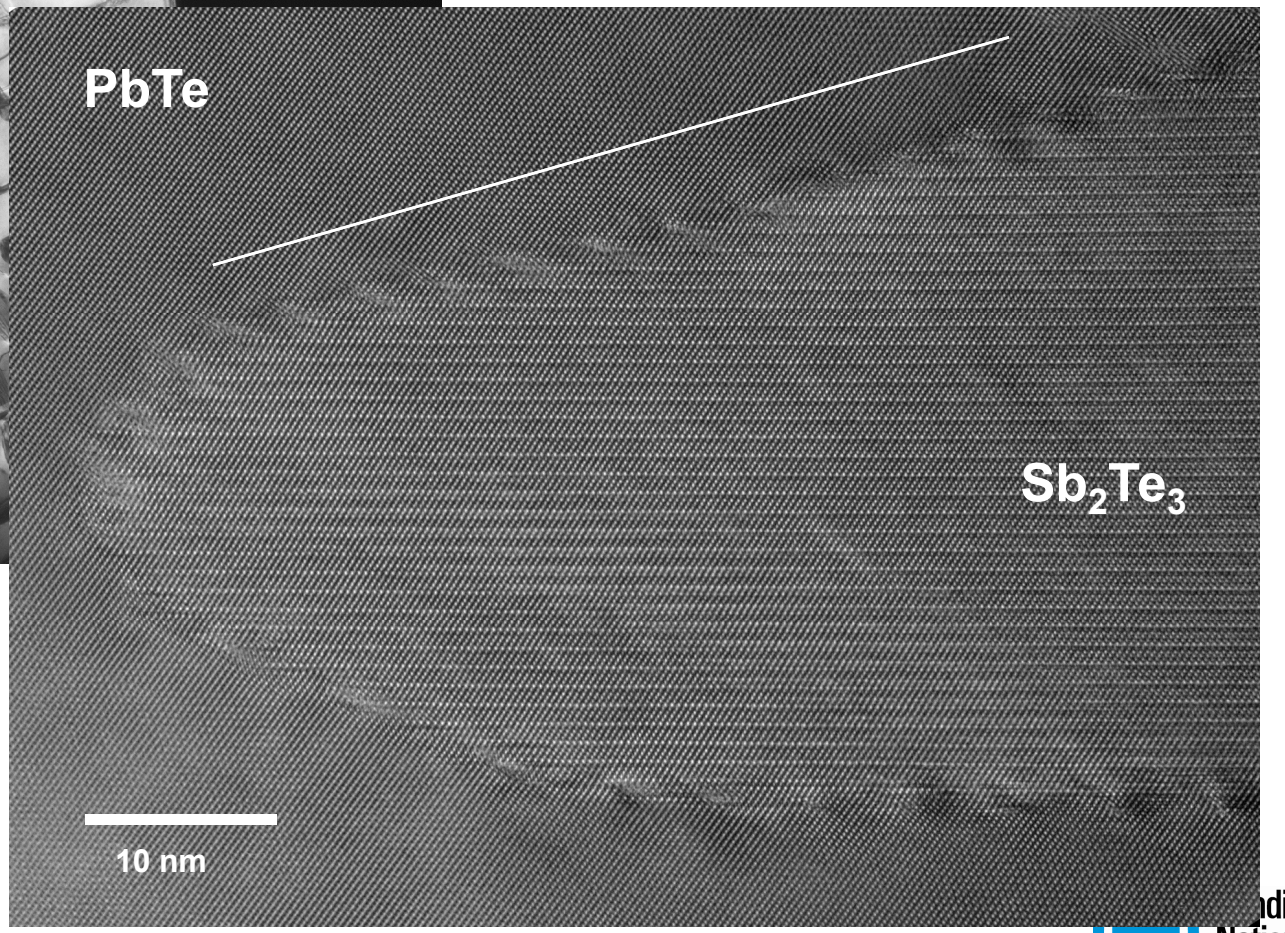
A system with larger misfit: $PbTe/Sb_2Te_3$

Sb_2Te_3 Precipitates in PbTe

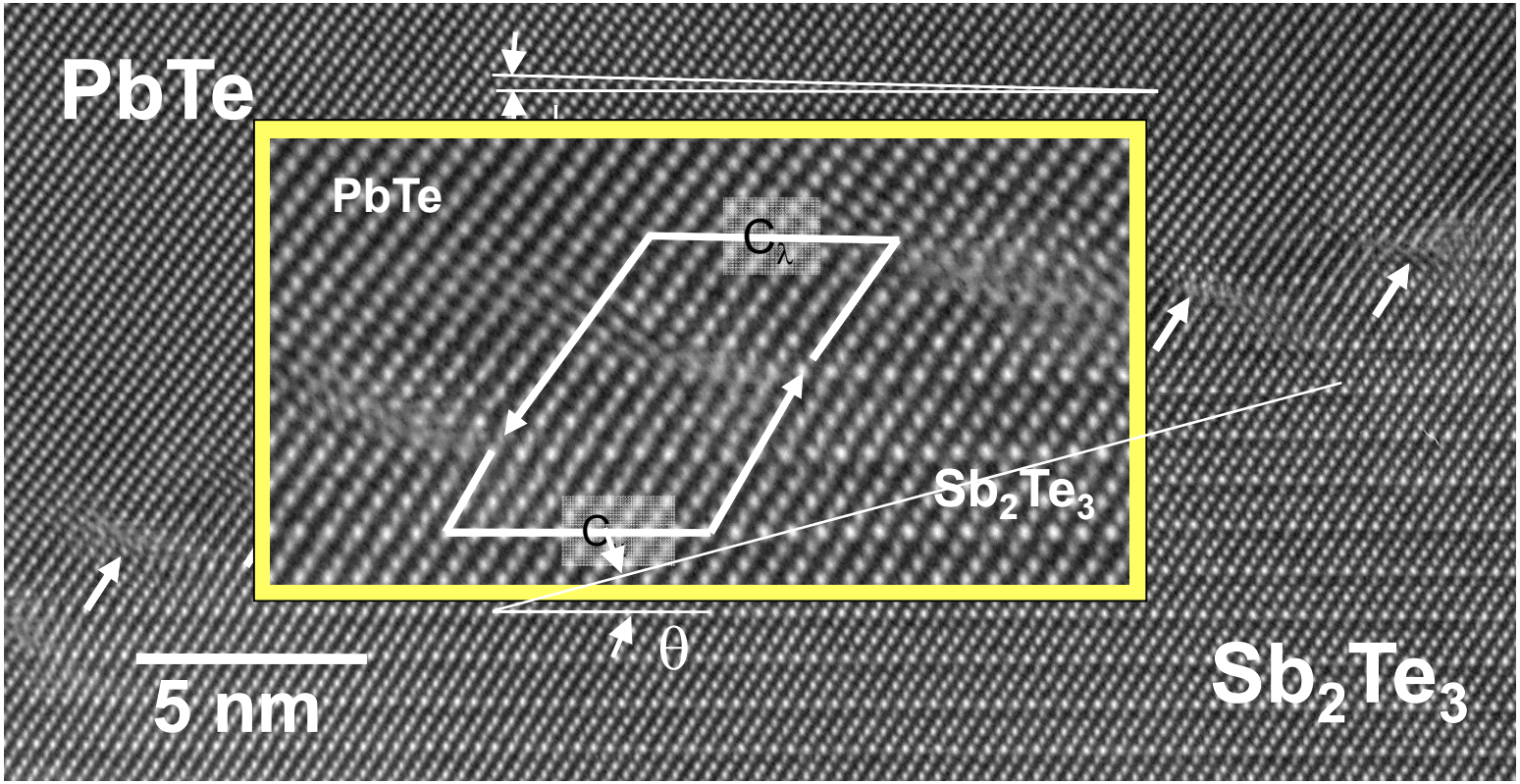


$AgSbTe_2(111)/Sb_2Te_3(0001)$
Misfit: +0.79%



Heinz, Ikeda, Snyder, Medlin, Acta Materialia (2011)

Inclined Section of interface Composed of Disconnections



HRTEM JEOL 4000EX

Circuit Analysis:

Defects identical to the "6/5" disconnections observed in $AgSbTe_2/Sb_2Te_3$

Interface Geometry:

Inclination: θ =14.8° Lattice rotation: ϕ = 1.1° to 1.4°

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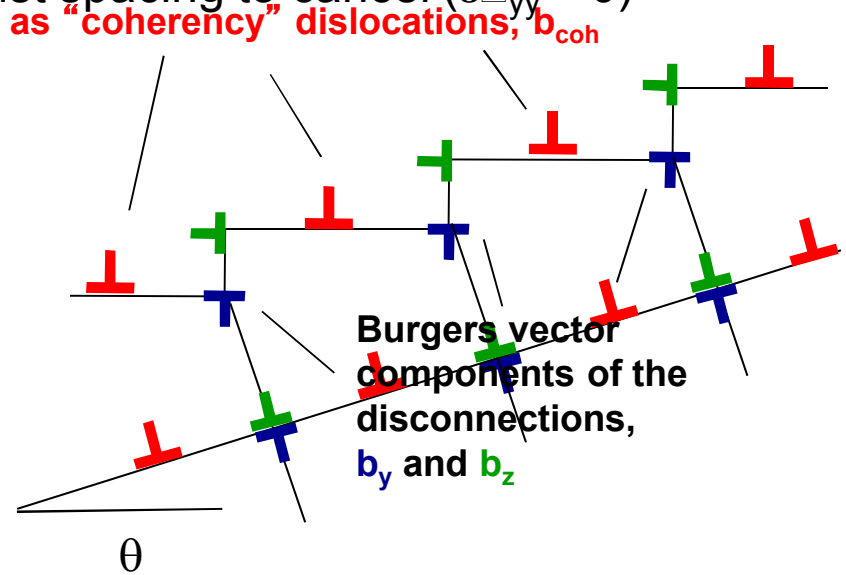
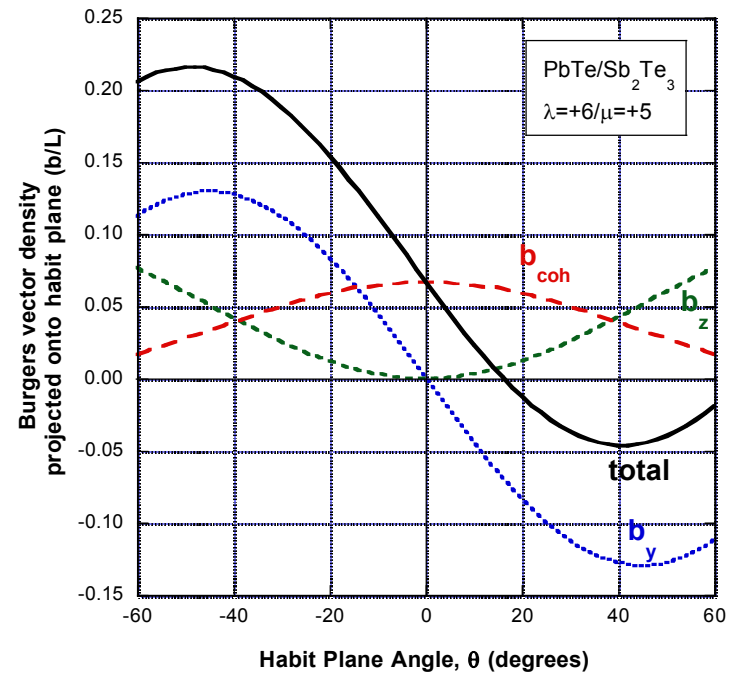
Interplay between Misfit Accommodation and Interface Inclination

Project components on inclined interface plane

Adjust spacing to cancel (ε_{yy} = 0)





$$-\varepsilon = (b_y \tan\theta + b_z \tan^2\theta)h^{-1}$$ ➔ θ=16.2°

Pond, Celotto, Hirth, Acta Mater. 2003

Out of plane **b** components produce small rigid body crystal rotation,

$$\phi = 2\sin^{-1}[(b_z\cos\theta - b_y\sin\theta - \varepsilon h\cos\theta)\sin\theta/2h]$$ ➔ ϕ=1.7°

Disconnection spacing accommodates the (111)/(0001) coherency strain.

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Conclusions

Key structural aspects of the tetradymite-type chalcogenides are manifested in the detailed structures of extended defects in these materials.

- Weak, van der Waals bonding across double chalcogenide layers
- Ability to accommodate non-stoichiometry through altering the layer stacking
- Close inter-relationship between the rocksalt and tetradymite structural types.

Attention to the topological properties and detailed structure of extended defects in the chalcogenides is critical.

- Understanding interfacial formation and stability and, ultimately, interfacial transport properties in nanostructured bulk thermoelectrics.
- Set of elementary "building blocks" for a general picture of interfacial structure in chalcogenide thermoelectrics

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Acknowledgements

Sandia/Livermore

N.Y.C. Yang, C.Spataru, K. Erickson, J.D. Sugar

Sandia/Albuquerque

M. Siegal, S. Limmer, W.G. Yelton

LBNL/NCEM

Q. Ramasse (present address, SuperSTEM Laboratory, Daresbury, UK)

California Institute of Technology

N.A. Heinz, T. Ikeda, G.J. Snyder

Special thanks to:

-LLNL: John Bradley, for use for LLNL's Titan 80/300 instrument
-LBNL: User program, National Center for Electron Microscopy
-UCD: Z. Zhang and E. Lavernia, for assistance with bulk Bi_2Te_3 processing

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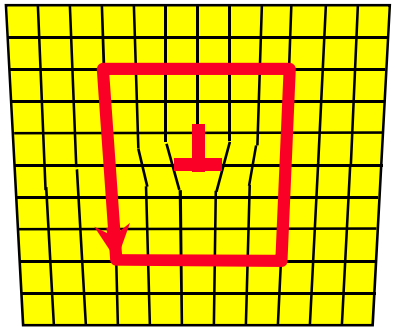
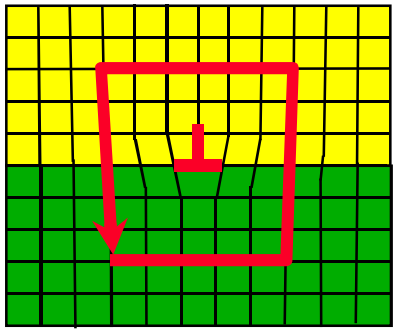
- EXTRA

Defining the topological properties of line defects requires a reference frame

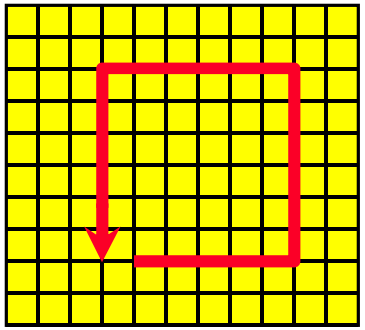
Bulk Lattice Dislocation.



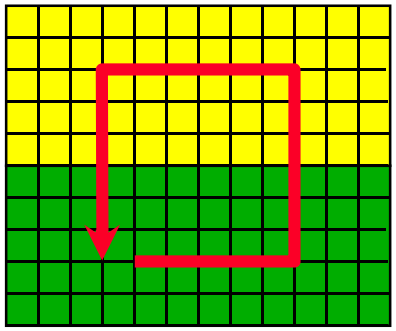
Heteroepitaxial Misfit Dislocation.



Reference Frame:
Perfect Crystal



Reference Frame:
Coherently Strained Interface



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Circuit analysis to quantify defect character

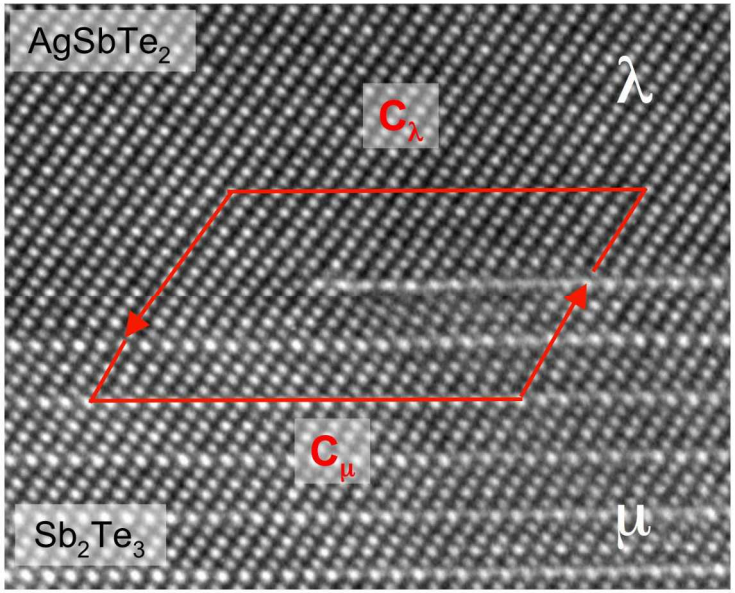
Burgers vector:

Upper crystal circuit

Lower crystal circuit

$$\mathbf{b} = -(\mathbf{C}_\lambda + \mathbf{P}\mathbf{C}_\mu)$$

Crystal coordinate transformation



Referenced to Coherent Frame:

Strain to bring μ and λ into coherency

$$P = LAM = \begin{pmatrix} \frac{1}{2} & \frac{-1}{2} & \frac{c_{hex}}{a_{cub}\sqrt{3}} \\ 0 & \frac{1}{2} & \frac{c_{hex}}{a_{cub}\sqrt{3}} \\ \frac{-1}{2} & 0 & \frac{c_{hex}}{a_{cub}\sqrt{3}} \end{pmatrix}$$

Converts from orthonormal to λ crystal coordinates

Converts from μ crystal coordinates to orthonormal coordinates

Misfit: 0.79%

$$r = \frac{1}{\sqrt{2}} \frac{a_{cub}}{a_{hex}} = 1.0079$$

Sb_2Te_3: a=4.264 Å
c=30.458Å

$AgSbTe_2$: a=6.078Å

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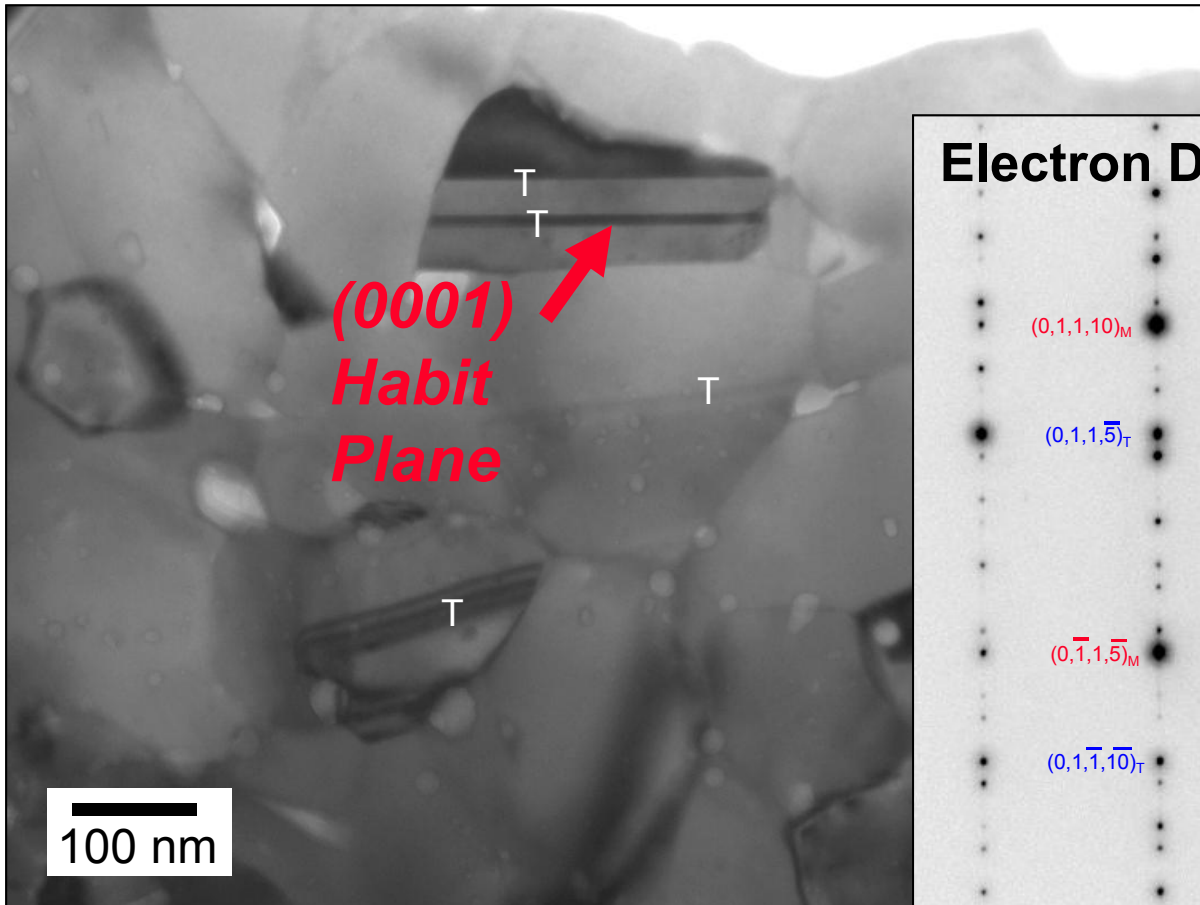
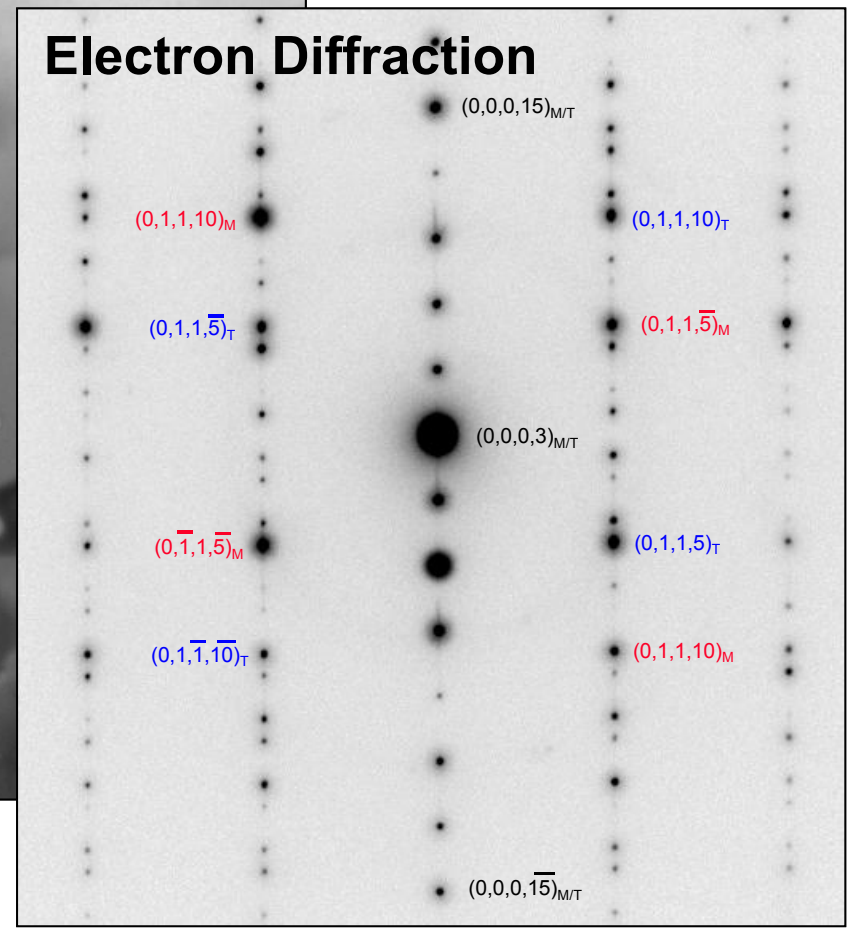
Twin microstructure and crystallography





Bi_2Te_3: Powder consolidated by spark plasma sintering

TEM Specimen Preparation:
Low voltage ion milling (1kV)
Cryo-cooling: <-100° C

Orientation Relationship:
(0001)//(0001)
[2-1-10]//[-2110]

180° rotation about c-axis

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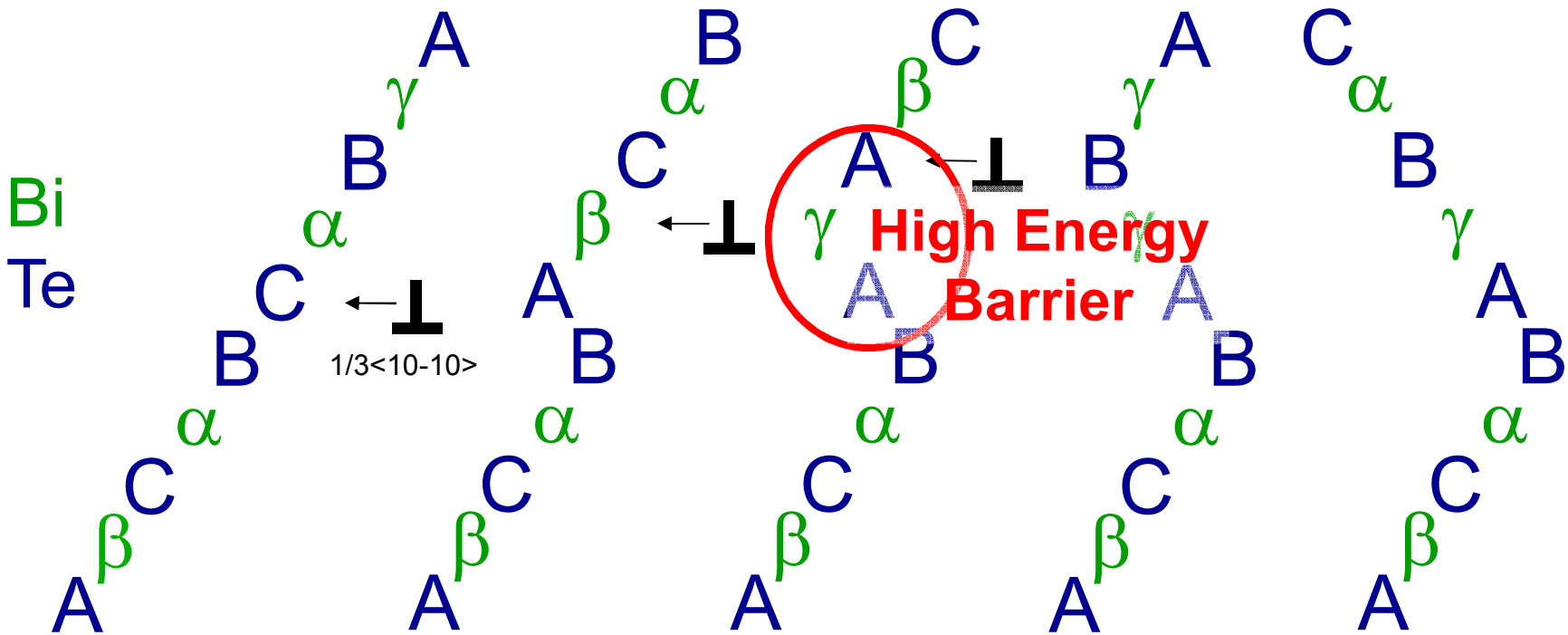
How do twins form in Bi_2Te_3?

Sequential motion of twinning dislocations?



-High energy barrier for Bi-terminated interface

➔ independent motion of twinning dislocations unlikely.

-Alternative: Coordinated defect motion.

Groupings of *unlike* twinning dislocations

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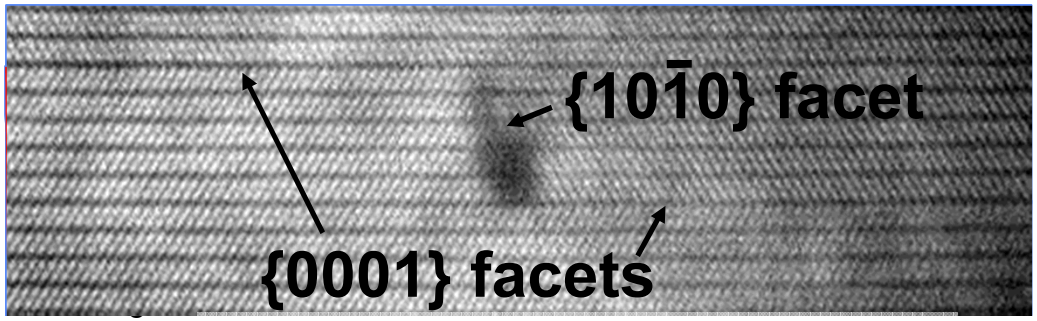
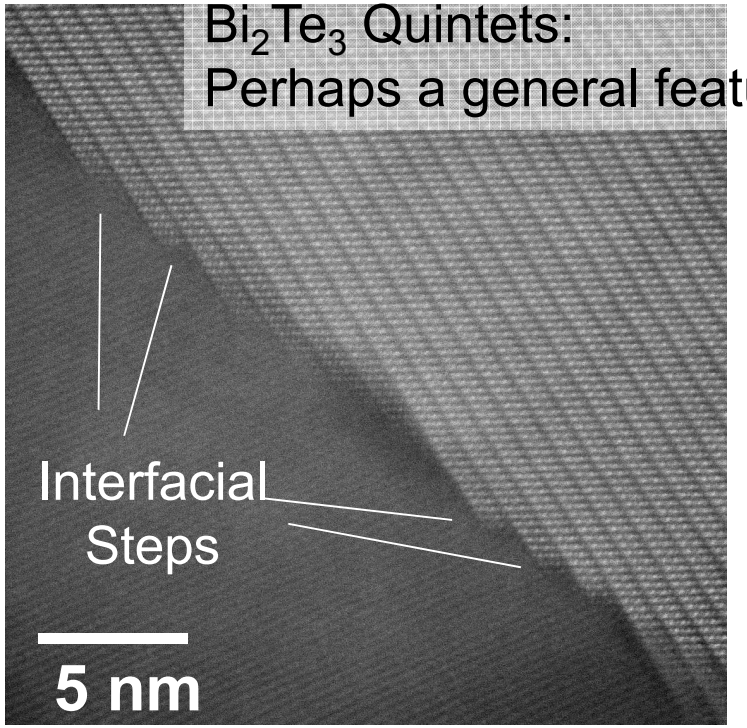
Steps in the Bi_2Te_3 Twin Boundary



5 nm

Steps of integral 5-plane Bi_2Te_3 Quintets: Perhaps a general feature?

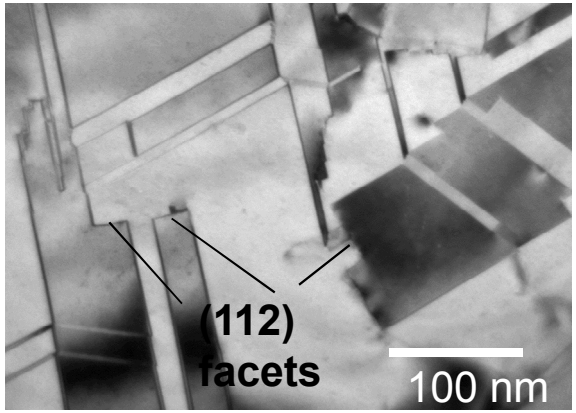


LLNL-Titan
HAADF-STEM 300 keV

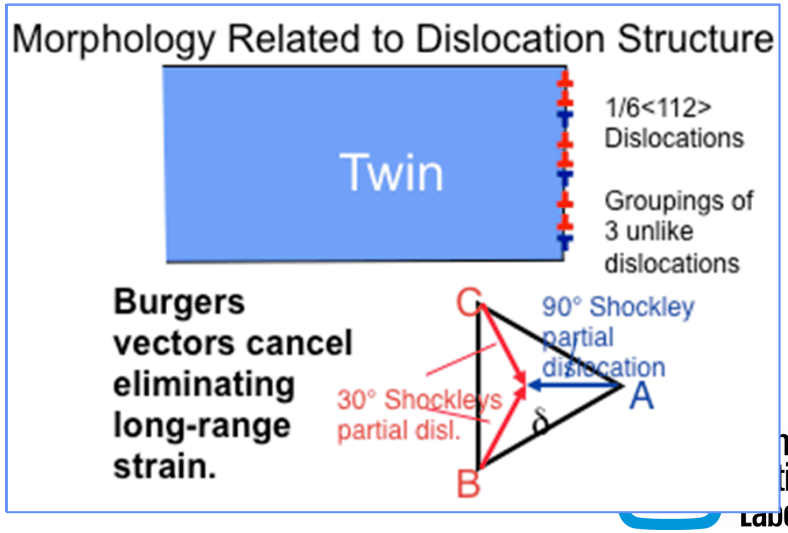
NBT20/21mar11/18.15.52

Morphology analogous to annealing and growth twins in FCC materials.

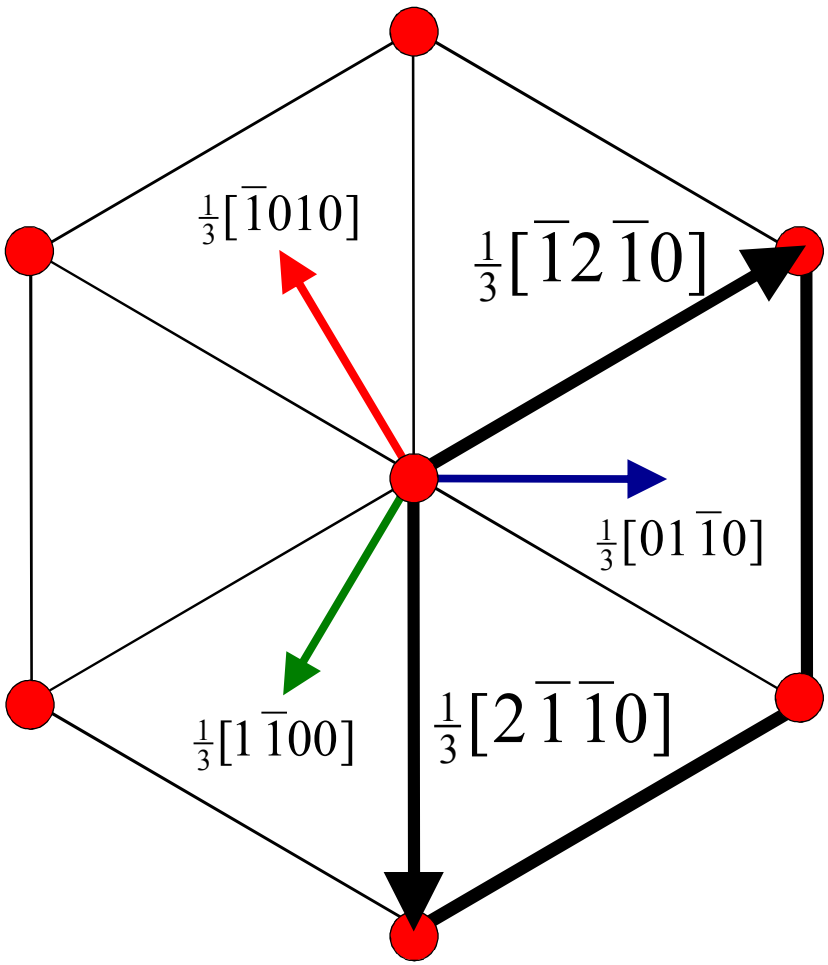
Example: Twins in Electrodeposited Ni

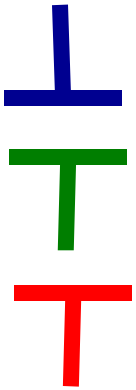


Lucadamo, Medlin, Talin, Yang, Kelly, Phil Mag 2005



Groupings of 3 allowed twinning dislocations in Bi_2Te_3 structue





Zero Net Burgers Vector

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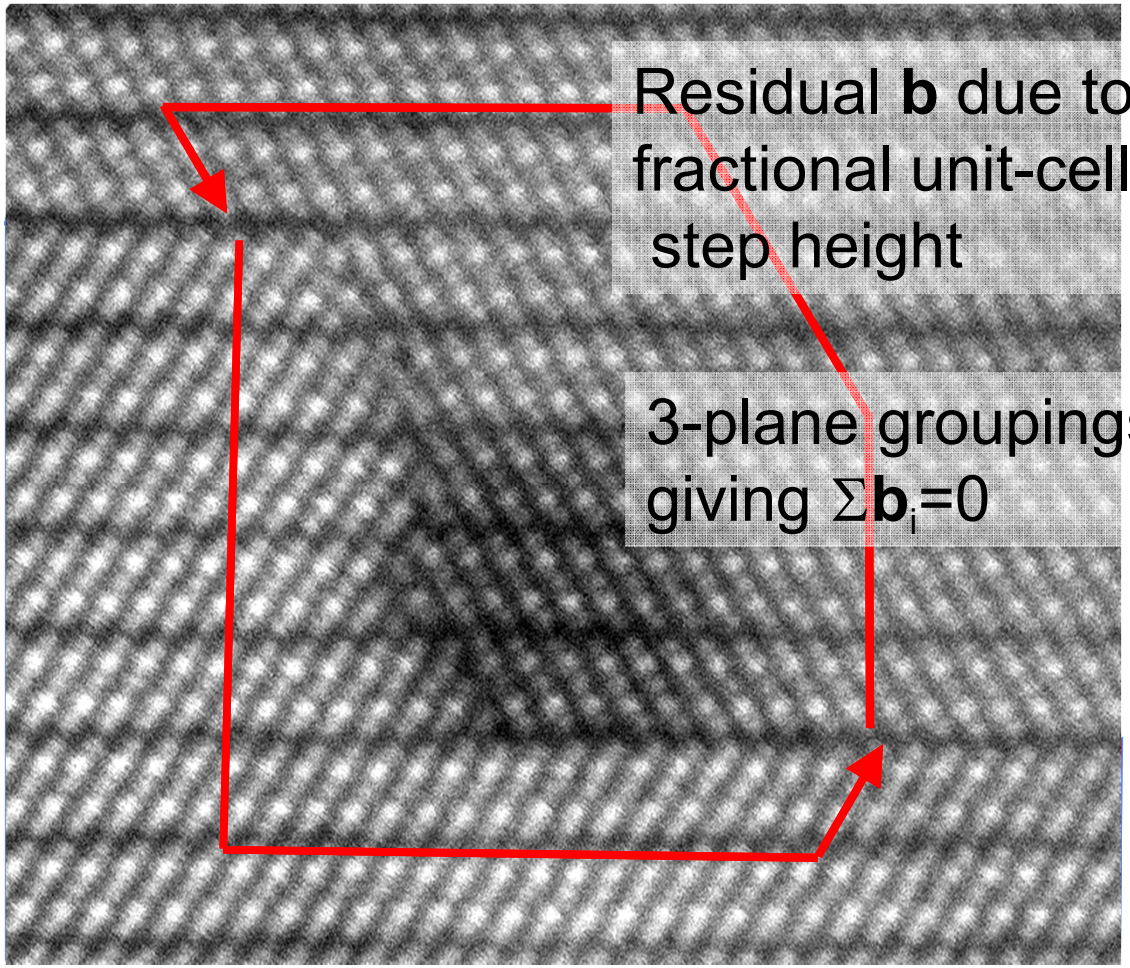
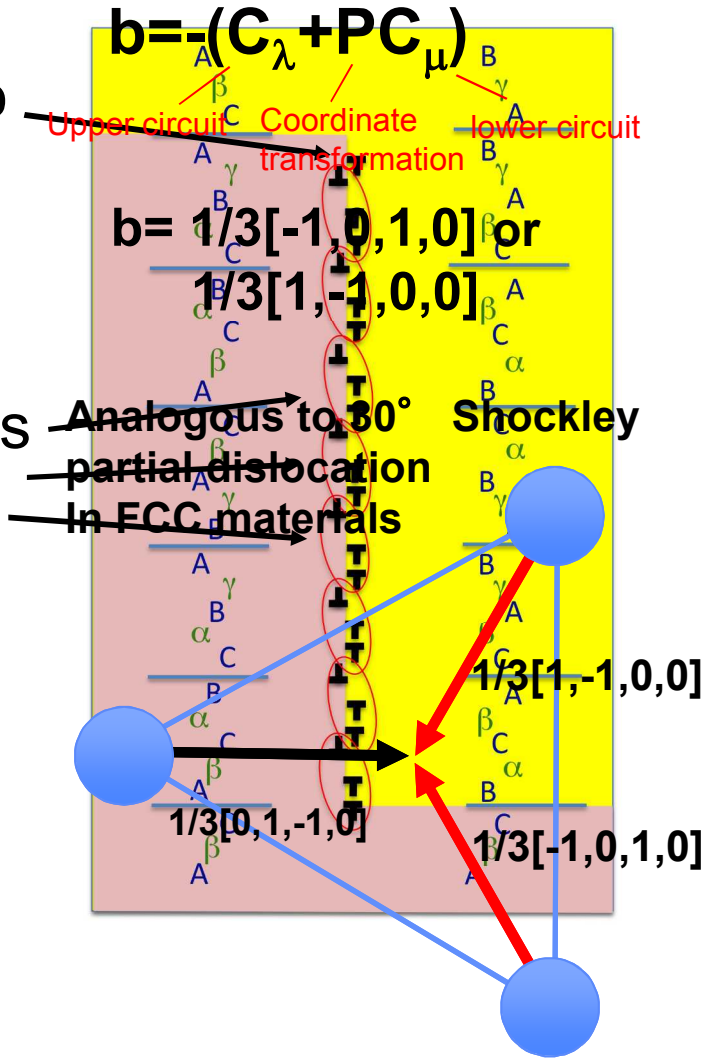
What is the dislocation content of the step?





LLNL-Titan
HAADF-STEM
300 keV

Medlin and Yang, Journal of Electronic Materials (2012)

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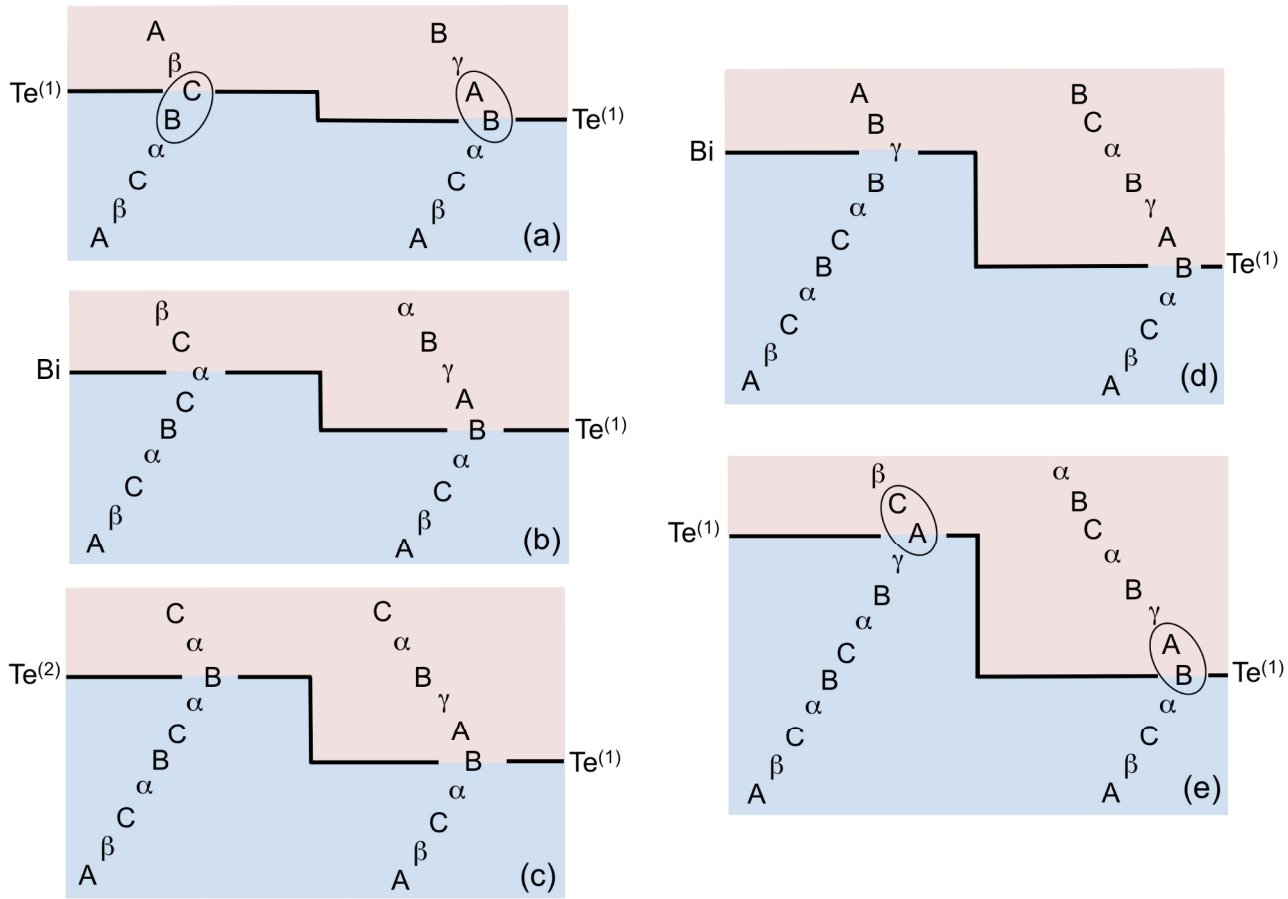
Consideration of other possible (0001) twin defects



Medlin and Yang, Journal of Electronic Materials (2012)

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Consideration of other possible (0001) twin defects

Step Height, h	Terminating Planes on Either Side of Step	Equivalency of Adjacent Twin Terraces	Burgers Vector, b
1	$Te^{(1)}/Te^{(1)}$	Equivalent (inverted)	$\frac{1}{3}\langle 10\bar{1}0\rangle$
	$Bi/Te^{(1)}$	Nonequivalent	
	$Te^{(2)}/Bi$	Nonequivalent	
2	$Te^{(1)}/Bi$	Nonequivalent	$\frac{1}{3}\langle 10\bar{1}0\rangle$
	$Te^{(2)}/Te^{(1)}$	Nonequivalent	
	Bi/Bi	Equivalent (inverted)	
3	$Te^{(1)}/Te^{(2)}$	Nonequivalent	0
	Bi/Bi	Equivalent (inverted)	
	$Bi/Te^{(1)}$	Nonequivalent	
4	$Te^{(1)}/Bi$	Nonequivalent	$\frac{1}{3}\langle 10\bar{1}0\rangle$
	$Bi/Te^{(2)}$	Nonequivalent	
	$Te^{(1)}/Te^{(1)}$	Equivalent (inverted)	
5	Same	Equivalent	$\frac{1}{3}\langle 10\bar{1}0\rangle$
10	Same	Equivalent	$\frac{1}{3}\langle 10\bar{1}0\rangle$
15	Same	Equivalent	0

Low Energy: $Te^{(1)}/Te^{(1)}$ termination.

Intermediate energy:

Termination at either Te site: $Te^{(1)}$ and $Te^{(2)}$

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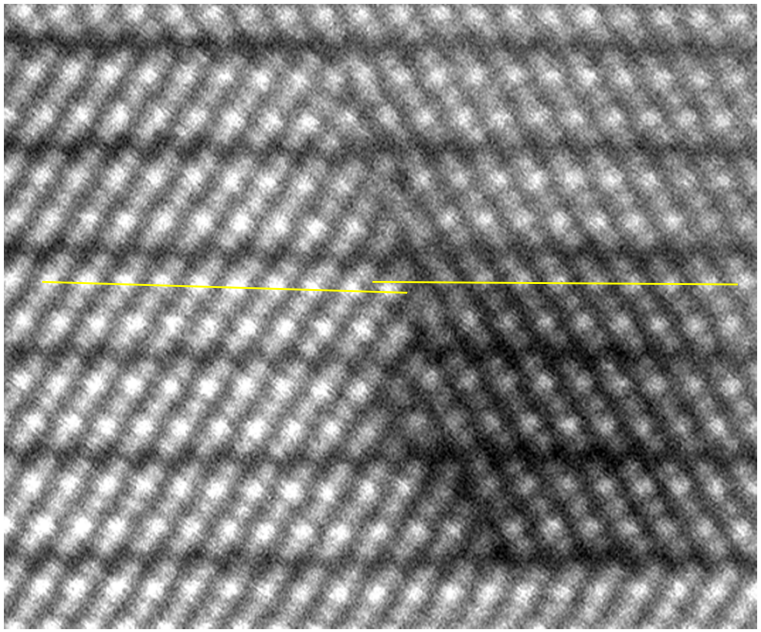
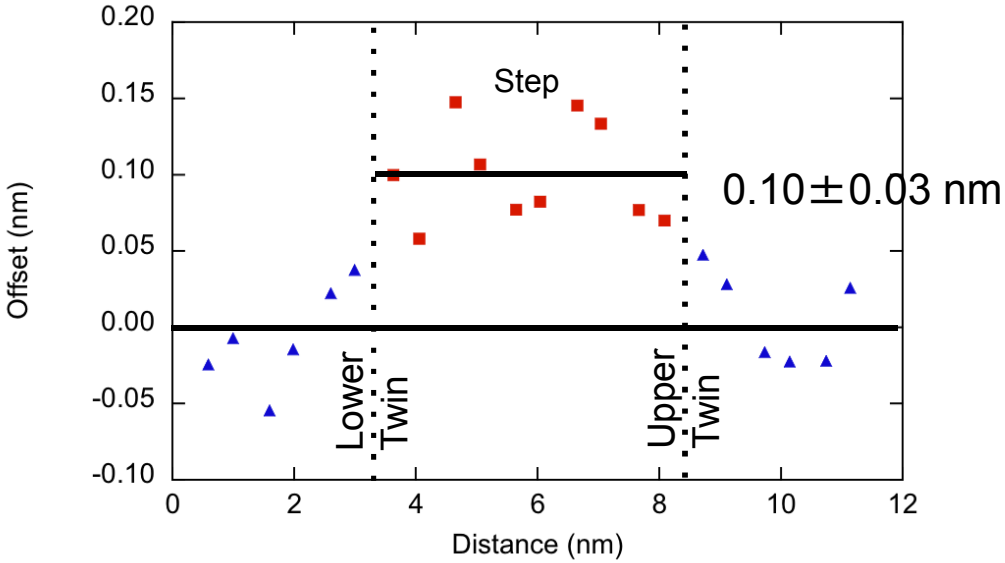
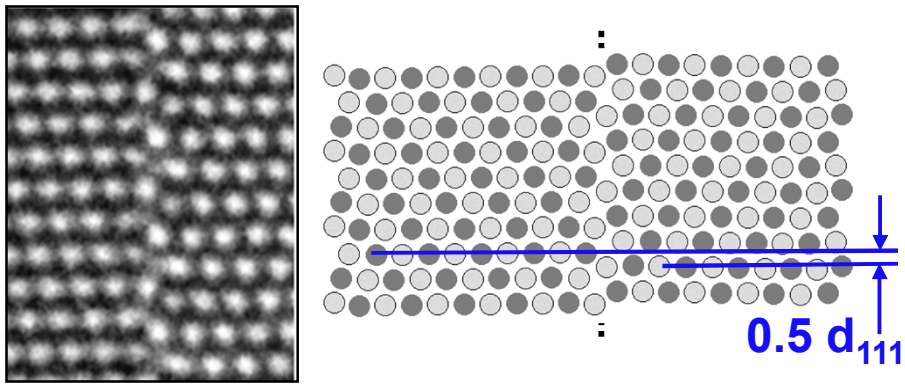
(0001) Planes are offset at step:





Offset similar to FCC {112} Twins
Example: Gold



Marquis, Hamilton, Medlin, Léonard, Phys. Rev. Lett. (2004)

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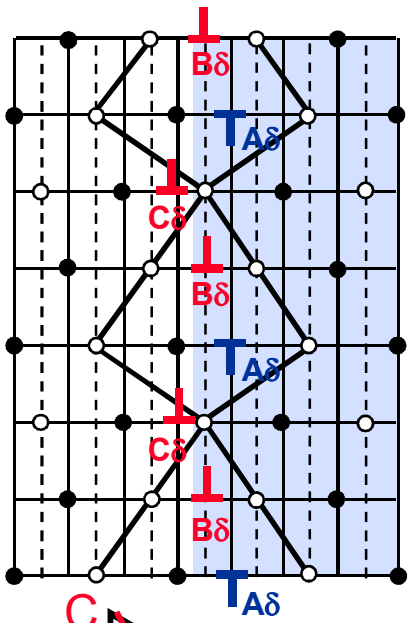
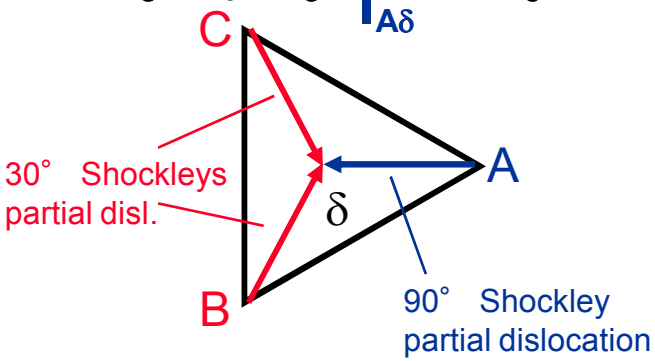
Grouping of 3 twinning dislocations is analogous to FCC {112} twin facets

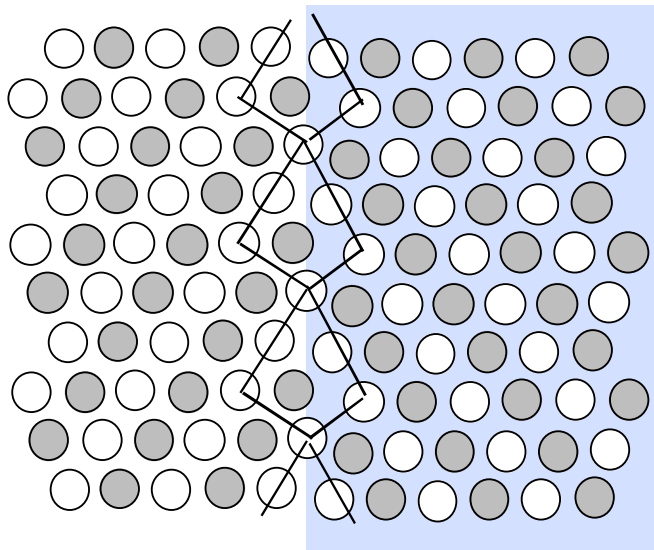
Example: Aluminum {112} Twin Structure:

Boundary dislocation arrangement

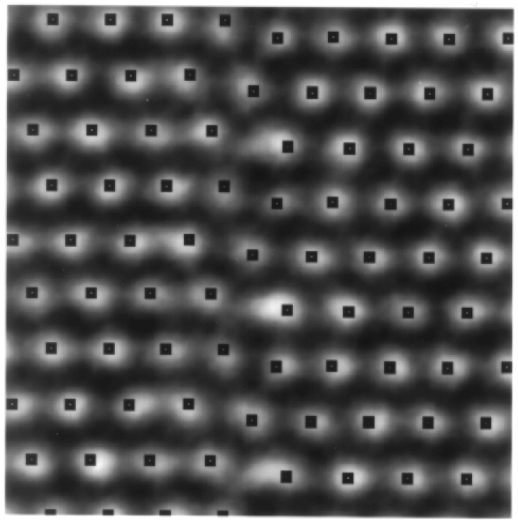




Relaxed Structure
(Aluminum-Voter & Chen EAM)



HRTEM



-D.L. Medlin, M.J. Mills, W.M. Stobbs, M.S. Daw, F. Cosandey MRS 295 (1993).
-D.L. Medlin, S.M. Foiles, G.H. Campbell, C.B.Carter,Materials Science Forum (1999).

Facile migration of {112} facets by coordinated motion of 3-layer groupings of 90° and 30° 1/6<112> dislocations

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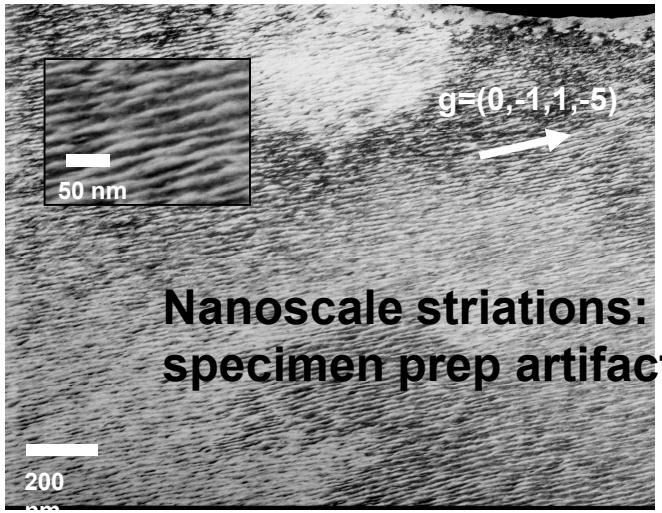
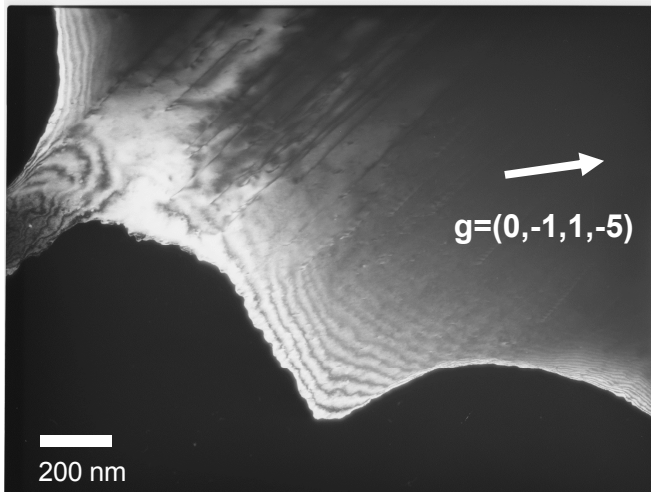
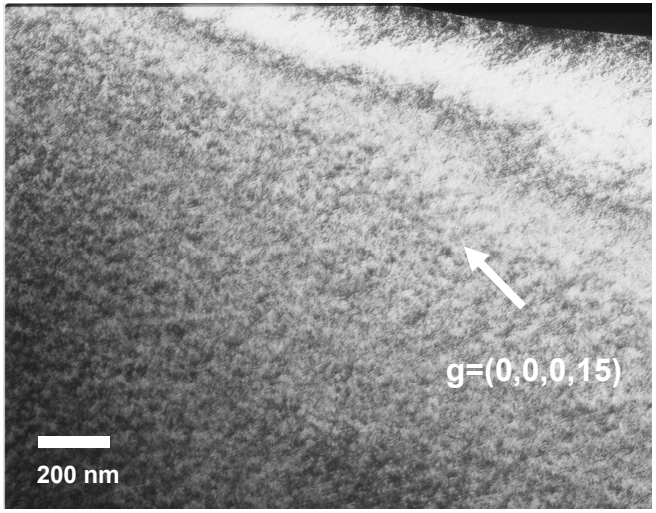
Aggressive ion-milling produces nanoscale artifacts in Bi_2Te_3

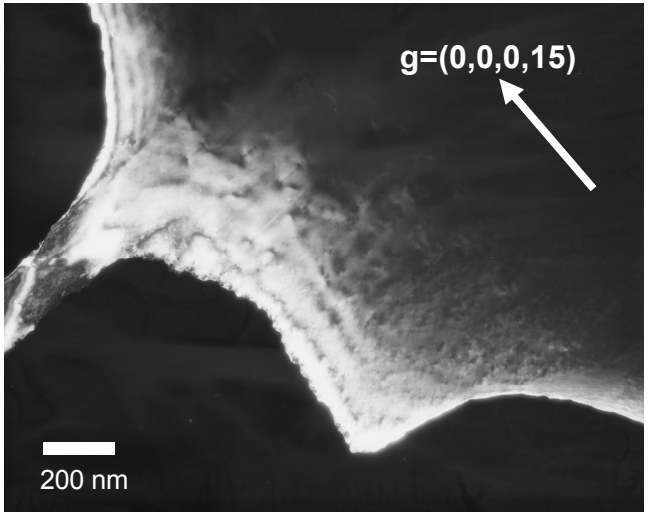
Ion Milled (Gatan DualMill 5 kV Ar+)



Electrochemical Polish







Can avoid artifacts using low-voltage, low-angle ion milling with cryo-cooling

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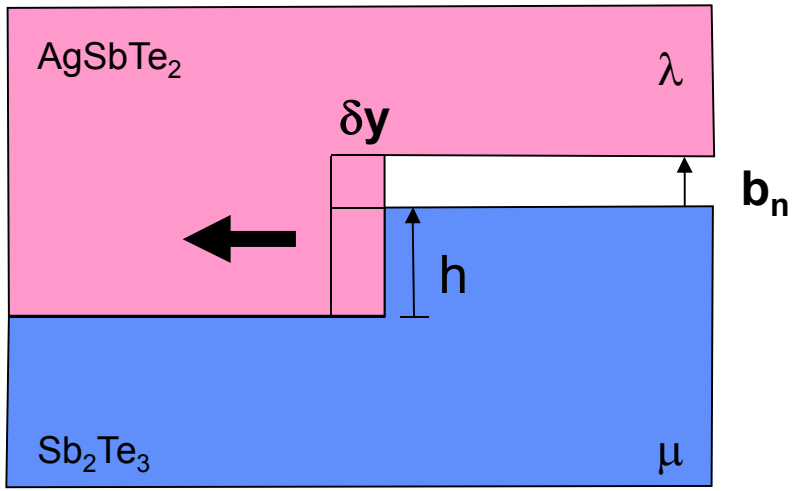
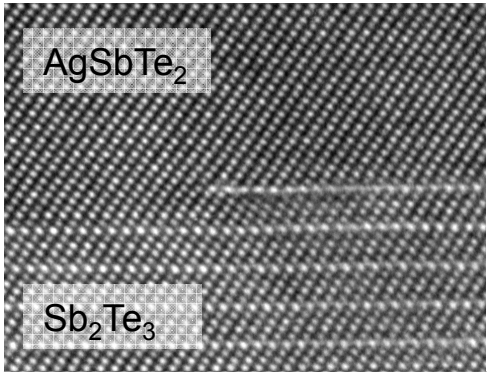
Defect properties give local mass flux required for transformation

Partition flux for defect motion into step and dislocation components





$$\frac{\Delta N_i}{L\delta y} = \underbrace{(\chi_i^{\lambda} - \chi_i^{\mu})h}_{\text{step}} + \underbrace{\chi_i^{\lambda} b_n}_{\text{dislocation}}$$

Hirth & Pond, Acta Mat 1996

Species	Step flux (atoms/Å²)	Dislocation flux (atom/Å²)	Total flux (atom/Å²)
Ag	$\frac{2}{3}\frac{c_{hex}}{a_{cub}^3}$ +0.09043	$\frac{2}{a_{cub}^3}\left(\sqrt{3}a_{cub} - c_{hex}/3\right)$ +0.00334	$\frac{2\sqrt{3}}{a_{cub}^2}$ +0.09377
Sb	$\frac{2}{3}\frac{c_{hex}}{a_{cub}^3} - \frac{8\sqrt{3}}{3a_{cub}^2}$ -0.03459	$\frac{2}{a_{cub}^3}\left(\sqrt{3}a_{cub} - c_{hex}/3\right)$ +0.00334	$-\frac{2\sqrt{3}}{3a_{cub}^2}$ -0.03126
Te	$-\frac{4}{a_{cub}^3}\left(\sqrt{3}a_{cub} - c_{hex}/3\right)$ -0.00668	$+\frac{4}{a_{cub}^3}\left(\sqrt{3}a_{cub} - c_{hex}/3\right)$ +0.00668	0

Reject Ag and Incorporate Sb in ratio of 3:1

Tellurium:
Step and Dislocation fluxes cancel.
No long-range Te transport required.

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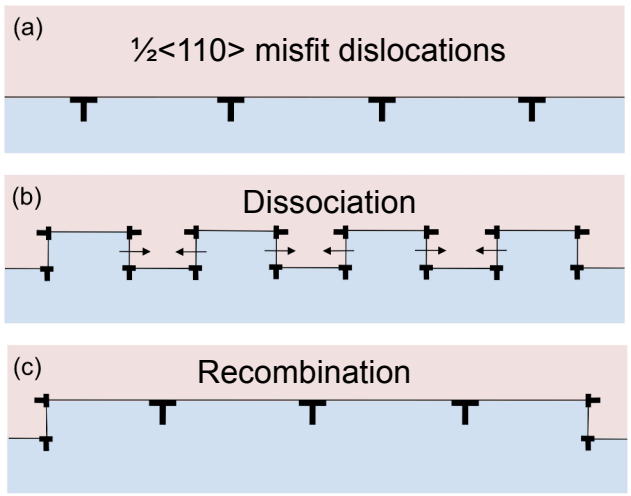
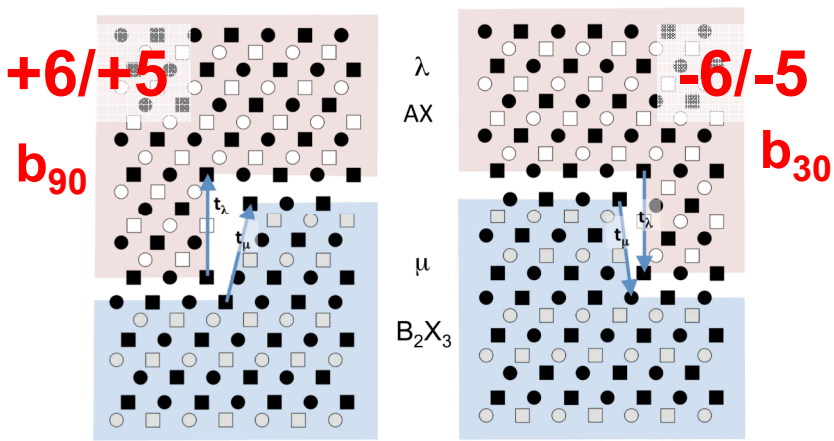
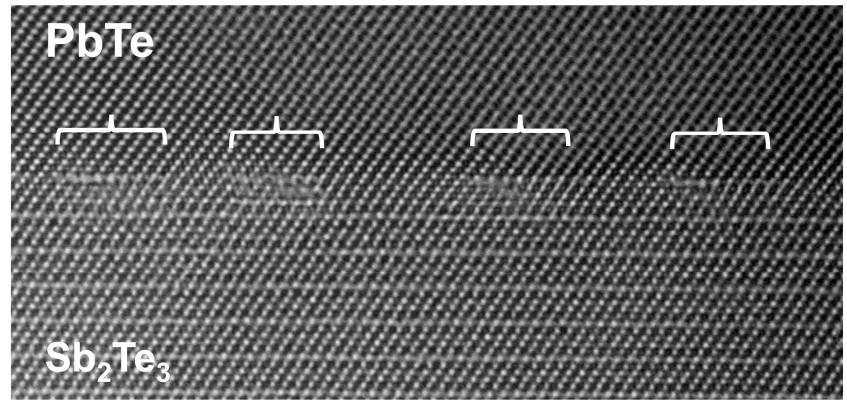
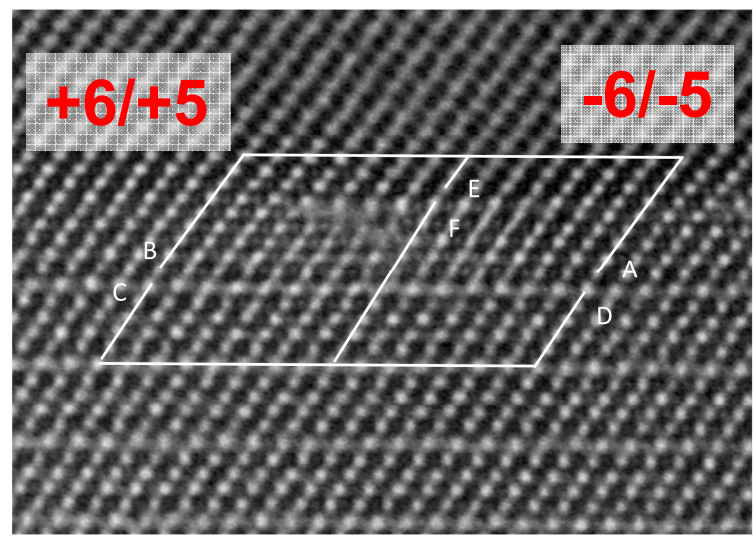
How might these defects form?

Dissociation of ½<110> misfit dislocations at flat sections of interface into disconnections









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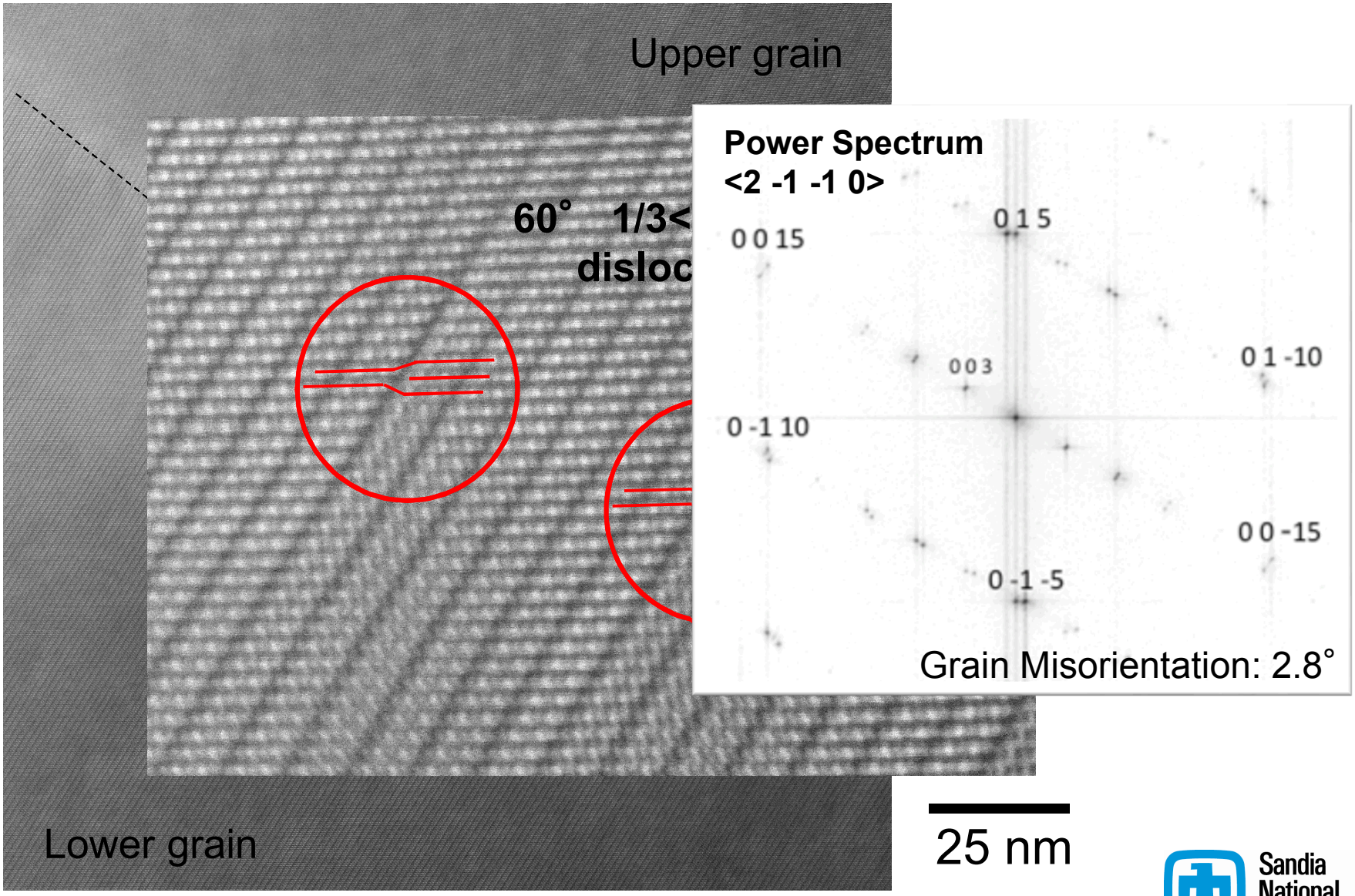
A Low Angle Tilt Boundary



STEM-HAADF

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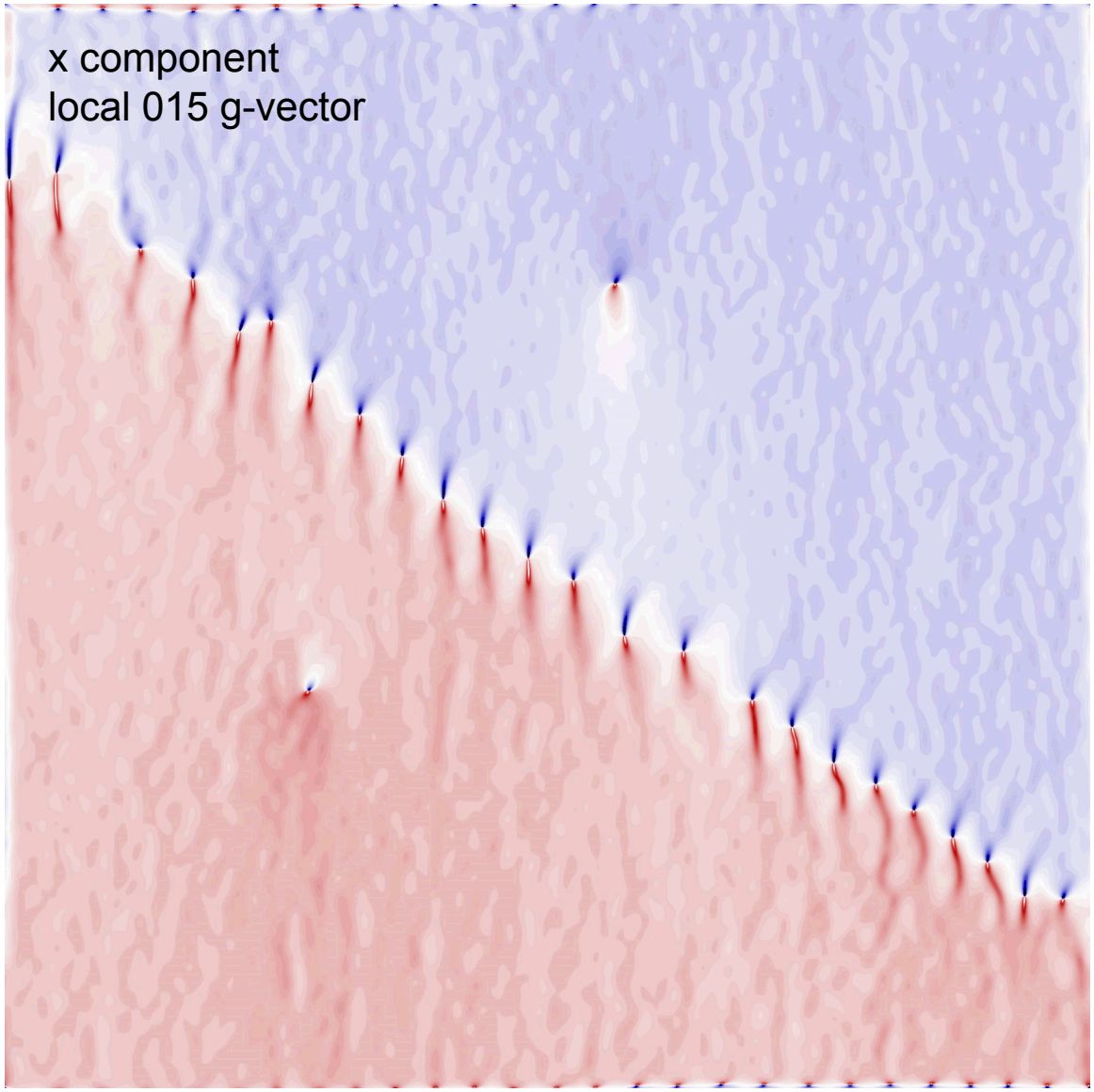
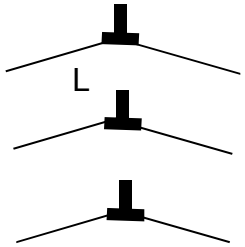
A Low Angle Tilt Boundary



Calculate tilt rotation from dislocation density

$$\theta = 2\sin^{-1}\left(\frac{b_{edge}}{2L}\right)$$

= 2.7° (calculated)
(2.8° measured)



L_{avg} = 8.0 nm

b_{edge} = 0.379 nm
(60° 1/3<2-1-10>
b=0.438 nm))

(for array of 60° dislocations, to be pure tilt, screw components must cancel)

25 nm

MacTempas Software. Geometric phase object routines: Hÿtch, Snoek, Kilaas, Ultramicroscopy 1998

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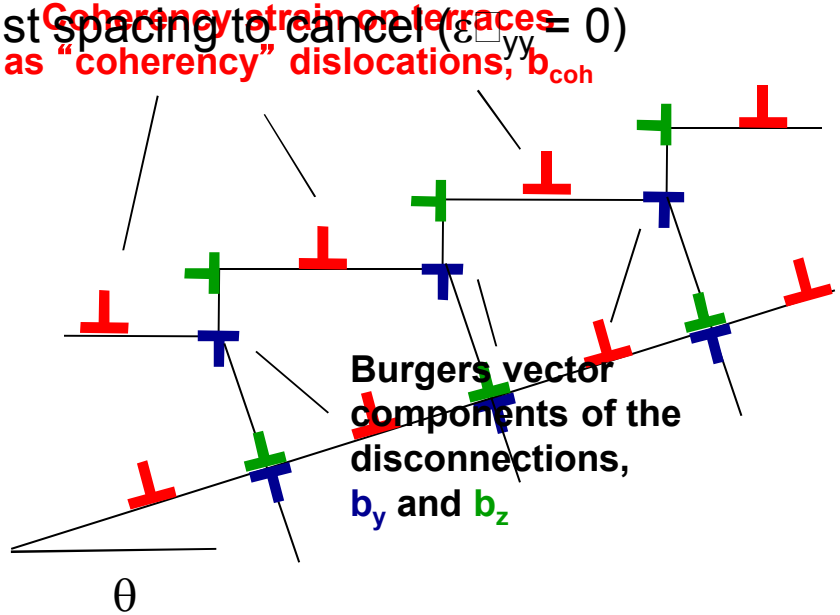
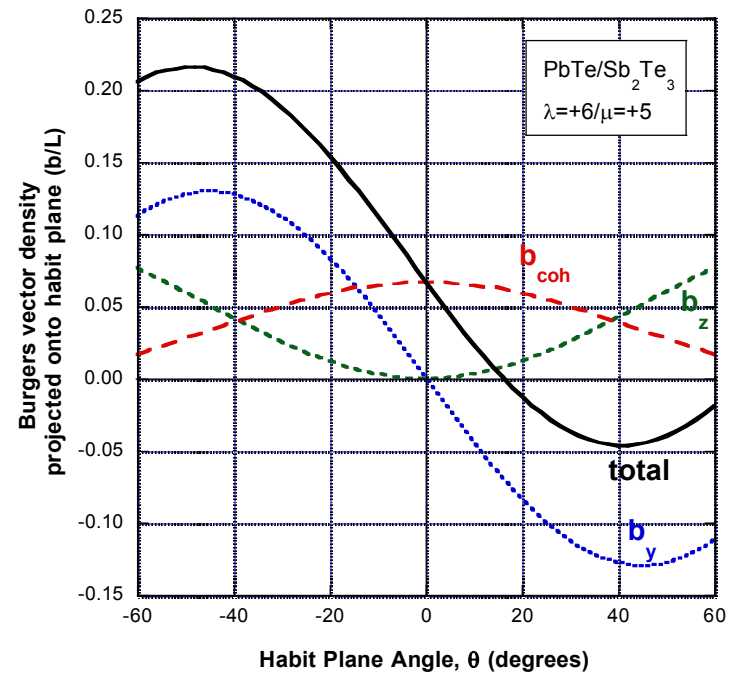
Interplay between Misfit Accommodation and Interface Inclination

Project components on inclined interface plane

Adjust spacing to cancel (ε_{yy} = 0)





$$-\varepsilon = (b_y \tan\theta + b_z \tan^2\theta)h^{-1}$$ ➔ θ=16.2°

Out of plane **b** components produce small rigid body crystal rotation,

$$\phi = 2\sin^{-1}[(b_z \cos\theta - b_y \sin\theta - \varepsilon h \cos\theta)\sin\theta / 2h]$$ ➔ ϕ=1.7°

Disconnection spacing accommodates the (111)/(0001) coherency strain.

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